

OLD DOMINION UNIVERSITY

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Norfolk, Virginia 23529-0456

DISTRIBUTION AND MANAGEMENT IMPLICATIONS OF CONTAMINANTS
IN ELIZABETH RIVER SEDIMENTS

Compilation of Recent Research on Sediment Contamination
in the Elizabeth River System.

Final Report

Prepared by

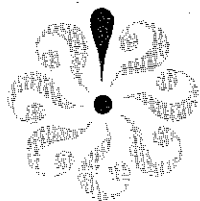
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Submitted to

Virginia State Water Control Board
2111 N. Hamilton Street
Richmond, Virginia 23230
Attn: Ms. Debra Trent

AMRL Technical Report No. 741-I

October, 1990
(Revised March, 1991)



This project was funded, in part, by the Virginia Water Control Board's Elizabeth River Initiative and the Virginia Council on the Environment's Coastal Resources Management Program through Grant No. NA89AA-D-CZ134 of the National Oceanic and Atmospheric Administration under the Coastal Zone Management Act of 1972 as amended.

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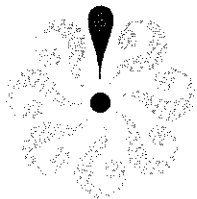
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*Appendices are bound separately as Volume II of this report.



DISTRIBUTION AND MANAGEMENT IMPLICATIONS OF CONTAMINANTS IN ELIZABETH RIVER SEDIMENTS

EXECUTIVE SUMMARY

The Elizabeth River system represents a major commercial and military resource to the Commonwealth of Virginia, as well as to the nation. Unfortunately, many of the shipping, industrial and urban activities associated with the seaport have created a highly polluted ecosystem. Such conditions represent potential sources of conflict with tourism and fisheries industries of the region. In response to this potential conflict, as well as to progress towards goals of the Clean Water Act in making the Elizabeth River "fishable and swimmable", the Virginia State Water Control Board (VWCB) has focused attention on identifying issues and management solutions related to the environmental quality of the River. One of the first steps toward the management of toxicants in the Elizabeth River involves identifying the distribution of contaminants introduced by point and non-point sources. The present study was designed to characterize the spatial patterns of various types of pollutants in the sediments so that "hot spots" can be targeted for more detailed studies and management actions. In addition, the design of the study allows an assessment of the "historical" temporal patterns of contamination in the system in two ways: 1) the depth distribution of contaminants provides a record of relative contamination over time; and 2) the selection of collection locations allowed the comparison of concentrations of

surface contaminants (i.e. those introduced by recent sources) to those observed in studies conducted 7-10 years ago.

In addition to the studies conducted under the original scope of work, this report summarizes the results of several other investigations of sediments in the Elizabeth River system conducted from February, 1989 to September, 1990. The results of a recently completed study of contaminant fluxes from the sediments, funded by the VWCB's Elizabeth River Long-term Management/Monitoring Program (ERLTM/MP) Phase II, are discussed in this document. A previously published technical report from Phase I of the ERLTM/MP, "Sediment Toxicity Assessments" (Alden, 1990), has been expanded and included in this report. Two other studies presented as Volume II of the original "Sediment Contaminant" report (i.e. report to VWCB dated June, 1990), "Pb-210 Geochronology" and "Grain Size Analysis of Cores from the Elizabeth River" are provided herein as appendices. Finally, management implications of the findings of all of the components of this report are discussed.

Spatial Patterns of Metal Contaminants

In general, the average concentrations of metals in the sediments were highest in the most industrialized portions of the Elizabeth River (i.e. vicinity of the shipyards in the Southern and Eastern Branches) and the concentrations decreased (for most metals) moving both upriver and toward the mainstem. In most cases the highest average concentrations of the metals were observed in

samples collected on the right shoal and the lowest in cores taken from the channel or, occasionally, on the left shoal. More specifically, most metals showed a pattern of regularly increasing concentrations moving up the Southern Branch from Site K to Site M, a distance of about 2 nautical miles. Clearly the most contaminated area in terms of metals in the sediments was Site M, where the highest, or near highest, average concentrations were observed for 8 of the 9 metals detected in the Elizabeth River sediments (Cd, Cr, Cu, Fe, Pb, Hg, Ag and Zn). The only exception to this pattern was seen for nickel which was observed at highest concentrations in sediments from the right shoal of Site Q.

The channel and left shoal of Site Q, a site in the Southern Branch in the vicinity of a power plant, were the River's least contaminated areas in terms of metal concentrations. However these results may have been influenced by dredging activities that occurred prior to sample collection.

The degree of metal contamination observed at Site J in the Elizabeth River mainstem was somewhat surprising. Although this site is situated in a less confined, presumably better flushed, area compared to the Southern Branch, the average concentrations of at least 5 metals (Cd, Fe, Ni, Hg, Ag) were within the range of those observed for these metals at sites in the lower Southern Branch.

One of the metals, selenium, was not found in detectable quantities (i.e. >8.3 mg/kg) in any of the sediment samples collected during the study.

Spatial Patterns of Organic Contaminants and Total Organic Carbon

Two compound classes stand out as dominating the organic contamination in the various depths and sites along the River system. These are the polynuclear aromatic hydrocarbons (PNAs) and the phthalates. However, other contaminants that do not fall into either of these chemical classes were also found in the River sediments. Site O (in vicinity of a creosote plant) stands out from the other sampling locations as being the most heavily contaminated with these chemical contaminants. Contaminant levels were typically lower in the channel sediments than in both of the transect shoals. However, the concentration does increase in the channel upstream, with a peak at Site O where the channel content is actually higher than both of the shoals. Patterns with depth appear to be site-specific, and often transect location-specific. Some trends do occur between neighboring sites such as the tendency for PNAs to decrease with depth in the left shoal and to increase with depth in the right shoal at sites K, L, and M.

Total organic carbon content was only moderate in Elizabeth River sediments, exceeding 5% at only one site in the Eastern Branch. The greater TOC content of these sediments may reflect the close proximity of this sampling location to marshes along the northern shore of the Eastern Branch. No other noteworthy spatial patterns in TOC data were observed.

Long-term Temporal Patterns

Comparisons were made between the concentrations of selected contaminants in sediments observed in the present (1989) study with those reported in previous studies. The sediment concentrations of seven metals (Cd, Cr, Cu, Fe, Ni, Pb and Zn) were compared between the 1989 data and a data set collected in 1979 as part of a U.S. Army Corps of Engineers (USACOE) study conducted by the AMRL. Likewise, the concentrations of 12 polynuclear aromatic hydrocarbons (PNAs) were compared between the 1989 data and that collected in a 1982 USACOE investigation conducted by the AMRL. Overall decreases in concentrations were apparent for most of the metals during the 10-year interval, but the majority of the organic (PNA) contaminants did not display general trends throughout the study area during the 8-year period between collections. Both the metals and organics data sets displayed regions where site-specific trends were apparent.

Among the metals, five (Cd, Cr, Fe, Ni and Pb) appeared generally to decrease in the sediments of the study area, while the other two metals (Cu and Zn) displayed no overall significant changes. Although the sediments of certain regions of the Elizabeth River remain highly contaminated with metals, the apparent decrease in many of the metals may be associated with pollution control actions and/or bans on certain uses of metals (e.g. the ban on lead in antifouling paints, widespread use of low lead gasolines, etc.). The observation that neither copper nor zinc displayed a pattern of decrease may reflect their continued

widespread use in shipping and shipyard activities (e.g. copper as the most common component of antifouling paints and the use of zinc in alloys and anti-corrosion devices). The temporal patterns of metals, both overall and regional, tended to be confirmed by the patterns observed with depth: sites or regions displaying a decrease in metals during the 10-year interval between collections also displayed an increase in concentrations with depth, suggesting that recent fluxes into the system were of lower magnitude than were previous inputs.

Two regions in the Southern Branch appeared to display increases in a number of metals in surface (more recent) sediments: Site M, right shoal, in the vicinity of a major shipyard; and Site N near the mouth of Paradise Creek. Although there are no extremely obvious sources of these metals for the latter station, they could be transported with suspended sediments from the more industrialized regions "downstream" (see below), or they could be associated with less obvious sources in the region (e.g. the "mothball fleet" near this station, runoff from the Paradise Creek drainage basin, etc.). Considering these trends and the high mercury concentrations observed in the surficial sediments of Site N, this region should be investigated further to determine the potential source(s) of the metals contamination.

Temporal decreases in metals concentrations in surface sediments were generally observed at sites near the confluence of the Southern Branch with the mainstem (Sites J, K and L). The relative concentrations of cadmium, chromium, lead, nickel and, to

a lesser extent, zinc tended to decrease from 1979 to 1989 in the sediments from this region. These temporal patterns were confirmed by increases in concentration with depth. A similar pattern was observed at sites in the upper reaches of the study area (Sites P and Q), but these trends may have been confounded by recent dredging operations.

The PNAs in sediments of the Elizabeth River continue to remain in high concentrations in certain regions of the Southern Branch (Sites K-Q). However, these contaminants displayed mixed temporal patterns throughout the study area: in some regions the surface sediment contamination tended to increase from 1982 to 1989, while in others, it tended to decrease. The most contaminated site (Site O), which was in the vicinity of an abandoned creosote factory, increased in heavy molecular weight PNAs but decreased in the lighter 2- and 3-ring organic compounds. This indicates that the site may continue to be a source of "weathered" creosote contamination. On the other hand, the sediments from the urbanized lower reach of the Southern Branch (Site K) increased in both low and high molecular weight PNAs, indicating active sources of petroleum/combustion contamination, possibly associated with shipping, marinas, shipyard activities and/or urban runoff. It should be noted that, until sediment transport patterns in the Elizabeth River are better understood, specific sources cannot be pinpointed by sediment contamination patterns alone. Rather, regionally-defined control strategies aimed at both point and nonpoint sources of the contaminants of

concern may be appropriate.

Contaminant Fluxes from the Sediments

Pilot flux studies were conducted on sediments taken from three sites in the mainstem, Eastern Branch and Southern Branch of the Elizabeth River. Laboratory flux experiments on sediment cores examined flux dynamics of organic contaminants, metals and ammonium across the sediment-water interface. Although the results are preliminary in nature and represent fluxes for conditions at three sites for one season (late spring), certain patterns were apparent.

Six PNAs (naphthalene, methylnaphthalene, phenanthrene, pyrene, fluoranthene and benzo(b)fluoranthene) were observed to flux from the sediment into clean water, but at moderately low rates (on the average, from 86 to 611 $\mu\text{g}/\text{m}^2/\text{day}$). The flux rates were related to the concentrations in the sediments and to the log P (octanol-water partition coefficient) of each contaminant. Numerical models that were developed to describe these relationships fit the empirical data quite well ($R^2=0.8$). These models can be used to calculate "rough cut" flux rates for various conditions when data are available for: the log P of the contaminants, the concentration in the sediments and the concentration in the water. These models indicate that it is highly unlikely that the few water quality criteria that are available for PNAs would be exceeded due to sediment fluxes alone. However, once validated, the models could be used to estimate the

magnitude of sediment efflux of organic contaminants as a source in loading inventories established as integral parts of control strategies.

Flux rates were also calculated for six metals: cadmium, copper, iron, manganese, nickel and zinc. Consistently undetectable water concentrations of silver, arsenic and lead prevented flux determinations for these three metals. Although somewhat variable, the fluxes of the metals were generally positive, indicating that, under the environmental conditions observed at the time of the experiment, the sediments were releasing metals to the water column. In general, the daily flux of metals represented 1-12% of the ambient load in the water column, producing doubling time estimates of 8-86 days for most metals. Considering the long residence of water in the Elizabeth River (1-2 months), these fluxes may be significant sources to the overall loading of the system. Seasonal changes may greatly influence the magnitude and even the direction of these fluxes, so additional investigations should be performed to determine flux rates under various environmental conditions before the contribution of sediment flux to the water column is estimated for loading inventories.

Ammonium fluxes were always positive and generally quite high. The average percent contribution to the concentrations in the water column ranged from 2-6%. Anoxic decomposition of organic matter in the organic rich sediments of the Elizabeth River is the source of the ammonium. Late summer conditions which are characterized by

high water temperatures and hypoxic or anoxic bottom waters may be expected to produce even higher flux rates, especially in the deep channel areas. Therefore, sediment fluxes of ammonium to the water column may be a significant nonpoint source. The actual flux rates for a variety of environmental conditions should be determined for loading assessments, particularly in regions where water quality criteria for this nutrient/toxicant are being approached or exceeded.

Sediment Quality Assessments

Data from Phase I of the ERLTM/MP were evaluated by several of the approaches most commonly used for sediment quality assessments: the Sediment Quality Triad, the Apparent Effects Threshold (AET) approach, and the Equilibrium Partitioning (EP) approach. The overall utility of the three approaches was also assessed by a series of computer simulation investigations employing data from the Elizabeth River.

Acute toxicity was not observed for the test organisms used and the sediments collected during the ERLTM/MP Phase I studies. However, the other two axes on the triad plots (sediment chemistry and in situ effects on benthic community diversity and biomass) did indicate moderate to high levels of "impact" at certain Elizabeth River sites relative to the characteristics of a reference site located in the lower Chesapeake Bay. The most "impacted" sites were: EBE1 (Eastern Branch) which displayed high ratio-to-reference (RTR) scores for sediment chemistry (organics and metals) and in

situ effects; SBE1 and SBE2 (Southern Branch) which were characterized by high RTR values for metals and organic contaminants; SBE3 which had high overall sediment chemistry and in situ effects RTR values; and WBE1 (Western Branch) which had high RTRs for metals and in situ effects.

No AET criteria could be calculated for the ERLTM/MP Phase I data set due to lack of apparent acute toxicity with the organisms tested. However, a comparison of sediment metals data to AET values which were calculated from previously collected Elizabeth River data indicated that AETs for one or more metals were exceeded by concentrations in sediments from the same areas that the Triad plots indicated were most "impacted": EBE1, EBE2, SBE1, SBE2, SBE3, and WBE1. Comparison of these AETs for metals to data from the present study on spatial distribution of sediment contaminants also confirmed that surficial (0-10 cm depth) sediment concentrations of metals exceeded AETs in samples taken from the lower reaches of the Eastern (Site EB) and Southern Branches (Sites K, L and M) of the Elizabeth River. The metals for which AET levels were most often exceeded were copper and lead. However, limitations/con-founding effects associated with the AET approach need to be taken into account in the interpretation of these patterns (see below).

Data from the ERLTM/MP Phase I studies were evaluated by the EP approach. Naphthalene, acenaphthene and fluoranthene were the only organic contaminants out of the numerous compounds observed in the sediments for which water quality criteria have been established, therefore, EP sediment quality "criteria" could only

be calculated for these contaminants. None of the sediment concentrations exceeded these EP "criteria". In fact, the maximum concentration of PNAs reported for the Elizabeth River would not have exceeded these "criteria", bringing the sensitivity of the EP approach into question (see below).

Evaluations of the three sediment quality assessment techniques identified a number of limitations/disadvantages in their application. The overall Triad approach was considered to be an important tool in the assessment of sediments since it incorporates three major components of sediment quality: sediment chemistry, sediment toxicity, and in situ effects. However, Triad plots as currently presented do not allow the display of confidence limits, so there is a potential for misuse/misinterpretation of these simplifying/summarizing visual displays. A computer simulation investigation has indicated that the Triad approach produced highly non-normal distributions of RTR values which are not amenable to the development of confidence limits by standard statistical techniques. The Triad approach may also produce high probabilities of type II error (i.e. the error of declaring an RTR value "non-impacted" when it is, indeed, taken from an impacted area) when applied to single samples. Therefore, it was recommended that Triad plots be used by managers for regulatory decisions only when the plots summarize the findings of comprehensive investigations with statistically validated conclusions. A bootstrap simulation approach was developed to produce confidence limits on Triad axes to allow managers the

ability to evaluate visually the degree of "confidence" that they can place in the patterns which are displayed by the plots.

The limitations of the AET approach were also presented and a simulation assessment was conducted to determine the effects of correlations between contaminants on the validity of AET based criteria. This assessment indicated that moderately high correlations ($r > 0.5$) produced a high probability of setting invalid AETs. Slightly higher correlations ($r > 0.6$) produced invalid AETs that could not be detected as being "false" even with large sampling efforts (up to 300 samples analyzed). As a result, it was recommended that AET based criteria, if used at all, be considered "first cut" levels of concern for identifying areas that display heavy sediment contaminant loads. Regulatory actions based upon AET criteria should be implemented only if validated by independent toxicological investigations.

Likewise, the apparent low degree of sensitivity associated with the values produced by EP models would indicate that EP based sediment quality criteria should not be used as the sole basis for compliance/remediation decisions. The observation that the most contaminated (and toxic) Elizabeth River sediments ever analyzed would not exceed the EP criteria for PNAs, strongly indicates that the models currently being considered are not very environmentally protective.

Since neither the AET nor the EP approaches produce completely defensible criteria for contaminants in sediments, alternate approaches to sediment quality assessments were proposed to involve

a first tier "screening" for toxicity followed by more comprehensive studies to determine the identity and sources of the contaminants responsible for toxicity for the purpose of control/remediation. Such an approach could be incorporated into the regulatory permit process to produce data bases for compliance and trend assessments.

Sediment History and Characteristics

A pilot Pb-210 geochronology study of four cores from the banks of the Elizabeth River indicated that these shallow areas are characterized by low sedimentation rates (0.8 to 2.4 mm/year) which appeared to increase in an upstream direction. Therefore, the shallow areas along the most highly industrialized areas of the mainstem and Southern Branch do not appear to be a major sink for particle reactive pollutants. However, the sedimentation rates within the navigational channel were reported to be much higher, suggesting that the channel may be a region of preferential accumulation of particle reactive pollutants.

Results of grain size analyses also indicated that the fine grain particles were being transported upstream, particularly along the channel. Although the fate of particle reactive pollutants that are transported by this non-tidal circulation is unknown, it is suspected that a major "sink" would be associated with the yet to be delineated turbidity maximum zone.

Management Implications of Elizabeth River Sediment Studies

Numerous management implications were associated with the

findings/observations of the studies presented in this report. As an organization framework for the presentation of these management implications, a schematic protocol was developed to describe the processes by which environmental managers could evaluate/assess sediment contamination issues. This protocol involved nine tasks in a decision-tree format. The implications that may be taken from the present study were identified as components of, or sources of information for, one or more of these tasks. A total of 45 management implications were discussed, although others (particularly of a site-specific or contaminant-specific focus) could be derived from the findings. The results of the present study and the ongoing Phase II ERLTM/MP should provide the basis for the direction of future management efforts concerning sediment contaminants in the Elizabeth River.



INTRODUCTION

The Port of Hampton Roads, Virginia is one of the largest industrial seaports on the eastern seaboard and is the largest military port in the world. In direct contrast to the commercial/military activities, the economy of the region is also supported by major tourism and fisheries industries. In addition, the condition of sensitive Chesapeake Bay ecosystems have also generated a great deal of concern. The concern over the Chesapeake Bay is representative of a broader national goal expressed by the Clean Water Act to make the nation's waters "fishable and swimmable". Cognizant of the potential conflicts between users of the various resources of the area, the Virginia State Water Control Board (VWCB) has mounted an effort to identify issues and management solutions related to the environmental quality of the Elizabeth River, the major deepwater channel of the Port of Hampton Roads.

The Elizabeth River, with a drainage basin of slightly over 500 km², is the principal deepwater shipping channel in the Hampton Roads area. The River has served as the focal point of industrial and commercial growth and development in the region. Along with the continuing growth and development of the region, the Elizabeth River has been the recipient of the associated pollution. The relatively small and infrequent input of freshwater and slight topographic relief of the area results in poor flushing of the system and hence the River acts as a sink for many toxic pollutants. A number of pollutant problems have been identified in

the River system. Chemical and biological assessments of the highly industrialized Southern Branch have revealed that it contains some of the most highly contaminated and toxic sediments in the country. Once in the sediments, this reservoir of contaminants may be released to the water and biota of the system and may represent a chronic source of pollution over the long term. Moreover, the patterns of sediment contamination indicate regional "hot spots" where toxic management actions may need to be focused.

The objectives of the study were:

1. to identify the major organic and metal contaminants in sediments of the Elizabeth River and to determine spatial distributions of these contaminants, both geographically and with depth in the sediment.
2. to compare concentrations of contaminants in surficial sediments with those observed in investigations conducted 7-10 years earlier.
3. to provide preliminary estimates of flux rates of organic and inorganic (metals and ammonium) contaminants from sediments to the water column of the Elizabeth River.
4. to provide an assessment of several approaches to the development of sediment quality criteria.
5. to describe the geological characteristics of the sediments from various locations in this system.

6. to determine sediment accumulation rates and sedimentation histories for representative regions of the Elizabeth River.

The overall goal of the project was to provide information which, when supplemented with data from other recent Elizabeth River studies and from the Elizabeth River Long-term Monitoring/Management Program (Phase II), can be used to develop strategies for the management (e.g. dredging and disposal options) of contaminated sediments.

In addition to the studies conducted under the original scope of work, this report summarizes the results of several other investigations of sediments in the Elizabeth River system conducted from February, 1989 to September, 1990. The results of a recently completed study of contaminant fluxes from the sediments, funded by the VWCB's Elizabeth River Long-term Management/Monitoring Program (ERLTM/MP) Phase II, are discussed in this document. A previously published technical report from Phase I of the ERLTM/MP, "Sediment Toxicity Assessments" (Alden, 1990), has been expanded and included in this report. The results of two studies addressing objectives 5 and 6 which were presented in a separate volume of the original "Sediment Contaminant" report (i.e. report to VWCB dated June, 1990), "Pb-210 Geochronology" and "Grain Size Analysis of Cores from the Elizabeth River", are again provided as appendices in Volume II of this report. Finally, management implications of the findings of all of the components of this report are discussed.



GEOGRAPHIC AND DEPTH DISTRIBUTION PATTERNS OF CONTAMINANTS IN SEDIMENTS OF THE ELIZABETH RIVER

METHODS

Sample Collection Locations

Sediment samples were collected from the Elizabeth River at 9 sites located at approximately one mile intervals, including one site in the mainstem near Hospital Point (Site J), one in the Eastern Branch near Colonna's Shipyard (Site EB), and seven in the Southern Branch between the Norshipco Berkley Plant (Site K) and the Virginia Power Chesapeake Facility (Site Q) (Fig. 1 and Table 1). At 8 of these sites, samples were collected from the mid-channel and from both sides of the channel on the "shoals" (i.e. the undredged area outside of the navigational channel). At the remaining station, Site P, a sample was collected only at mid-channel since the U.S. Army Corps of Engineers is proposing to widen the channel (i.e. shore to shore) in this portion of the Southern Branch during the Elizabeth River deepening project.

Box core samples were collected on May 23, 1989 at six locations in the Elizabeth River (Sites J, K and M and 3 sites in the vicinity of Site O) for the purpose of assessing sediment accumulation rates in the River using radiogeochemical techniques. Complete details of this study are reported in Volume II, Appendix A (Pb-210 Geochronology) of this report.

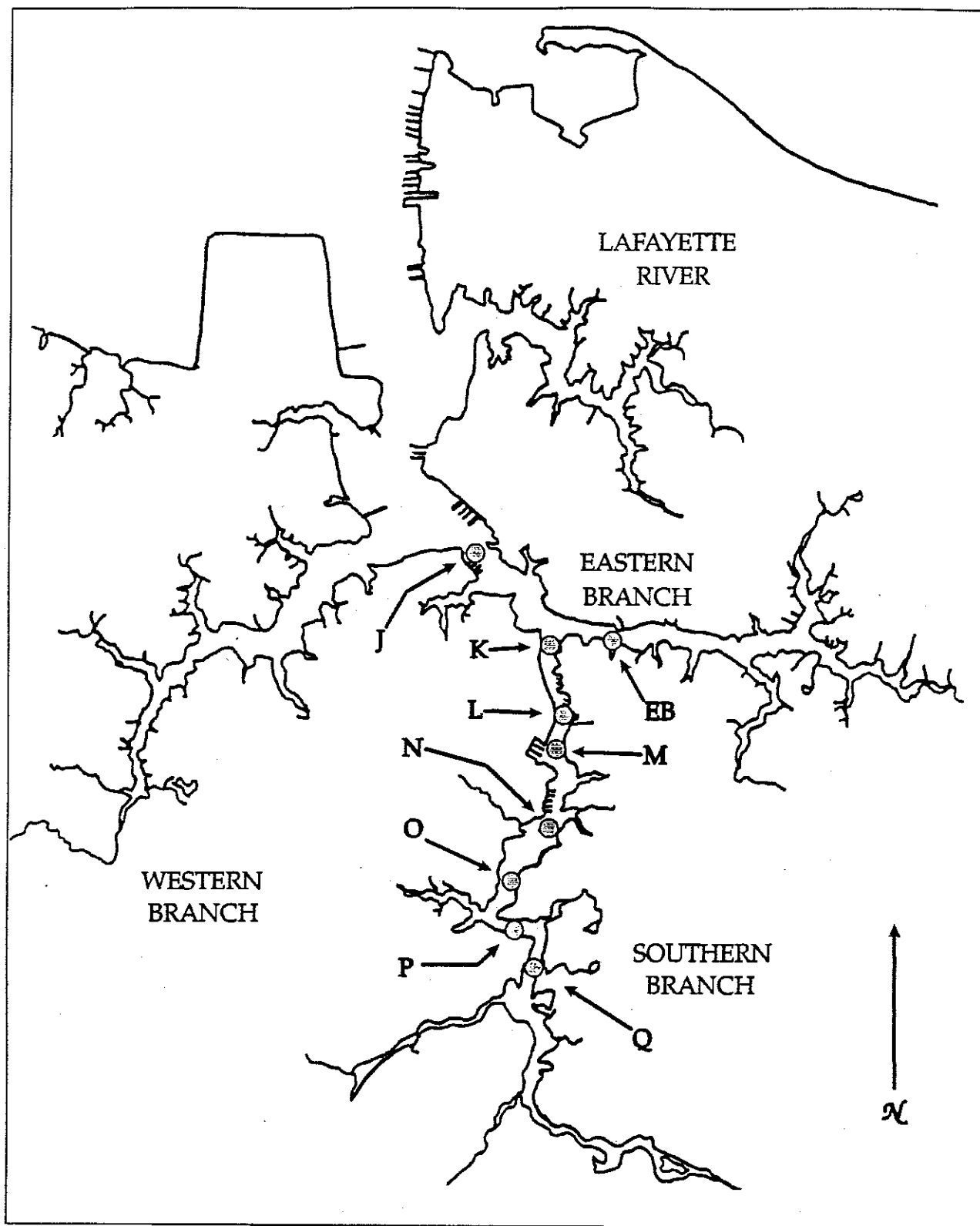


Figure 1. Map of the Elizabeth River system showing sediment sampling sites.

Table 1. Sampling site locations (chart coordinates) for the Elizabeth River Sediment Contaminants project, May 1989. "Right Shoal" refers to the site location to the right of the channel when facing upstream.

Station	Sampling Location		Right Shoal	River Mile Designation ¹	Municipal/Industrial Point Source(s) In Vicinity ²
	Left Shoal	Channel			
J	36°51'13"N 76°18'15"W	36°51'08"N 76°18'17"W	36°51'02"N 76°18'22"W	ELI006.37	Portsm. City, Ballard Fish Co., J.H. Miles
K	36°50'19"N 76°17'32"W	36°50'19"N 76°17'38"W	36°50'20"N 76°17'44"W	SBE000.045	Norshipco Berkley
L	36°49'34"N 76°17'29"W	36°49'32"N 76°17'31"W	36°49'32"N 76°17'35"W	SBE000.99	Mobil Oil Co.
M	36°48'47"N 76°17'22"W	36°48'47"N 76°17'28"W	36°48'52"N 76°17'43"W	SBE001.87	Norfolk Nav. Shipyard, Chevron USA
N	36°47'53"N 76°17'28"W	36°47'54"N 76°17'32"W	36°47'55"N 76°17'36"W	SBE002.875	Atlantic Wood, Texaco
O	36°47'03"N 76°18'12"W	36°47'04"N 76°18'15"W	36°47'06"N 76°18'18"W	SBE004.10	HRSD, Lonestar Ind., Eppinger & Russel
P	36°46'40"N 76°18'06"W	36°46'37"N 76°18'07"W	36°46'35"N 76°18'07"W	SBE004.96	Swift Chemicals
Q	36°46'12"N 76°17'45"W	36°46'13"N 76°17'49"W	36°46'15"N 76°17'53"W	SBE005.76	Vepco, Weaver Fert., Smith Douglas Fert.
EB	36°50'25"N 76°16'35"W	36°50'22"N 76°16'32"W	36°50'19"N 76°16'32"W	EBE000.98	Colonnas Shipyard, Miller Oil Co.

Notes:

¹ "Channel" location

² Information provided by VWCB

Sample Collection and Field Processing Procedures

Several attempts were made in late April-early May, 1989 to collect sediment samples using a gravity corer. This coring method was abandoned when it was determined that the sampling device could not penetrate deeper than about 100 cm into the sediment. A local contractor was then employed to collect the sediment samples with the use of a vibracorer. Sample collection was completed on May 28, 1989. Upon retrieval of each sample the PVC core liner containing the sediments was capped at both ends and removed from the sampler and a new liner was inserted into the coring tube. The sediment core was then partitioned into the depth fractions specified by the Scope of Work (Shoals: 0-10, 10-30, 30-70 and 70-150 cm; Channel: 0-30 and 30-150 cm), capped at both ends, marked with the appropriate sampling information (station, depth fraction, etc.), and stored on ice until returned to the laboratory.

Laboratory Processing and Analytical Procedures

All core samples were placed in freezers immediately upon return to the AMRL. The samples were thawed on June 1, 1989 and each core sample was homogenized in a stainless steel bowl prior to subsampling. The mixing bowl was acid-washed and thoroughly rinsed with Milli-Q water between samples in order to prevent cross contamination of the sediment fractions. Subsamples (a total of 328) were then taken from each depth fraction for distribution to the participating laboratories for analysis.

Sedimentary Analyses: Samples were analyzed for mean grain size, percents sand, silt and clay and percent water. In addition, the box core samples collected for the radioisotope study were examined by X-radiography. Details of this study, including all methodologies are presented in Appendix B.

The specific methodologies used for the laboratory preparation and analysis of the sediment samples are detailed in Appendix C (as SOPs: Standard Operating Procedures).

Metal Contaminant Analyses: Sediments were analyzed for ten metals (cadmium, chromium, copper, iron, lead, mercury, nickel, selenium, silver and zinc) by inductively coupled plasma emission spectrometry (ICP) and/or graphite furnace atomic absorption spectrophotometry (GF/AAS).

Organic Contaminant Analyses: Samples were analyzed by gas chromatography/mass spectrophotometry (GC/MS) to identify and quantitate the USEPA base-neutral and acid extractable "priority pollutants".

Total Organic Carbon Analysis: Samples were analyzed for total organic carbon (TOC) with the use of a carbon analyzer.

RESULTS AND DISCUSSION

METAL CONTAMINANTS

General Comments

This section of the report discusses the spatial patterns (i.e. geographic and depth distributions) of 10 metal contaminants (Table 2) in the sediments of the Elizabeth River.

Figures 2-11 illustrate the distributional patterns of metals over all sites and their respective transect locations (i.e. shoals and channel). Each of the values plotted on these graphs represent the concentration which would exist in sediments from a core for which the four depth sections had been composited. Therefore, the values represent mean concentrations, per kilogram of dry sediment, for a 0-150 cm composite core from a particular site. The values were calculated using the volume of each core section, its conversion to dry weight in grams using a specific gravity of 1.3 Mg/m³ (an estimate for sandy muds from Brady, 1984), and the mean percent dry solids for all sites for a particular core section depth (see Table 3). By employing this approach the concentrations determined in each core section were "weighted" based on both the percent dry solid material and the volume contribution of each core section to the entire 0 to 150 cm core.

Table 2. List of metal contaminants analyzed and their detection limits.

<u>Metal</u>	<u>Detection Level</u> <u>(mg/kg)</u>
Cadmium	0.5
Chromium	0.5
Copper	1.0
Iron	0.5
Lead	5.0
Mercury	0.1
Nickel	0.5
Selenium	8.3
Silver	0.5
Zinc	0.25

Table 3. Mean percent dry solids and standard errors by core depth.

<u>Core Depth (cm)</u>	<u>Percent Dry Solids*</u> <u>(% of total weight)</u>
0-10	48.9 ± 3.0
10-30	53.4 ± 3.2
30-70	52.5 ± 2.1
70-150	56.0 ± 2.1

*Dry solids refers to the fraction of the total sediment sample remaining after evaporation and subsequent drying at 120°C to a constant weight.

The metals data are also presented by depth interval within each core sample (Figs. 12-21). All metal concentrations are reported as mg/kg dry sediment or parts per million (ppm).

Overall Spatial Patterns

In general, the average concentrations of metals in the sediments were highest in the most industrialized portions of the Elizabeth River (i.e. vicinity of the shipyards on the Southern and Eastern Branches) and the concentrations decreased (for most metals) moving both upriver and toward the mainstem (Figures 2-11). In most cases the highest average concentrations of the metals were observed in samples collected on the right shoal (i.e. the western or southern side of the River) and lowest in cores taken from the channel or occasionally on the left shoal. More specifically, all metals showed a pattern of regularly increasing concentrations on the right shoal moving up the Southern Branch from Site K (mouth of the Southern Branch) to Site M (off a major shipyard). However, on the left shoal of this section of the River, the concentrations of 5 of the metals were greatest at Site K (off a shipyard) and decreased moving toward Site M.

Clearly the most contaminated area in terms of metals in the sediments was Site M in the Southern Branch, where the highest, or near highest, average concentrations were observed in the channel and right shoal for 8 of the 9 metals detected in the Elizabeth River sediments.

The channel and left shoal of Site Q, a Southern Branch site in the vicinity of a power plant, appeared to be the River's least contaminated areas in terms of metal abundances. However, these results may have been influenced by dredging activities that occurred prior to sample collection. The noticeable exception to this low contamination pattern was seen for nickel, which was abundant (i.e. at the highest observed concentration in the study) on the right shoal at Site Q.

The pattern of metal contamination in the Eastern Branch (Site EB) was generally comparable to the industrialized regions of the Southern Branch, with concentrations of all metals in shoal sediments noticeably higher than found in the channel.

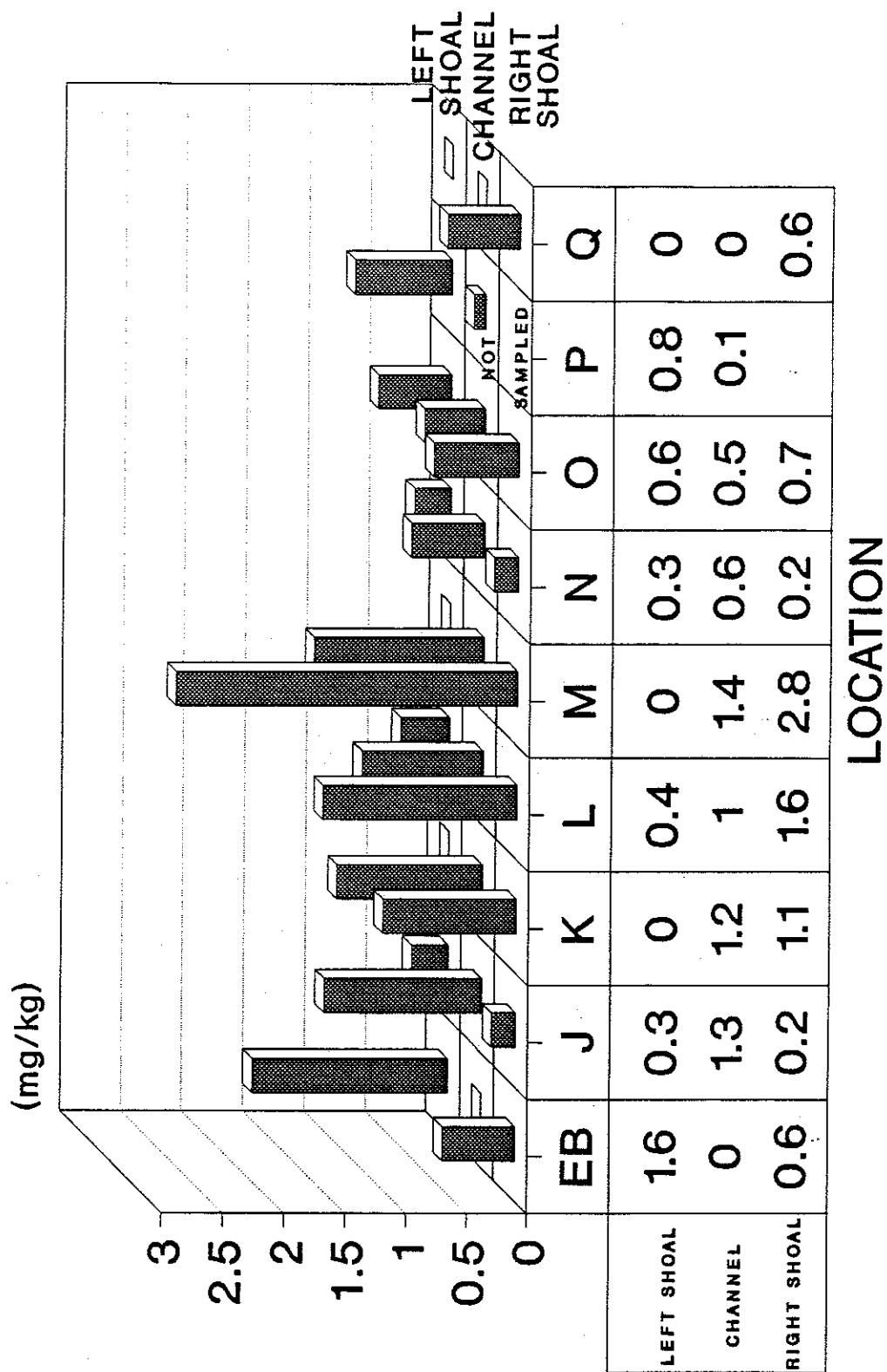
The degree of metal contamination observed at Site J in the Elizabeth River mainstem was somewhat surprising. Although this site is situated in a less confined area compared to the Southern Branch, and with presumably better tidal flushing, the average concentrations of at least 5 metals (Ag, Cd, Fe, Hg, Ni) were within the range of (and sometimes higher than) the concentrations observed for these metals in the lower Southern Branch (Sites K-M).

One of the metals, selenium, was not found in detectable quantities (i.e. >8.3 mg/kg) in any of the sediment samples collected during the study.

Figure 2. Cadmium concentrations in Elizabeth River sediments by site and transect location. Values represented by each bar are the concentrations averaged across all depth fractions of the core sample to a depth of 150 cm.

Figure 3. Chromium concentrations in Elizabeth River sediments by site and transect location. Values represented by each bar are the concentrations averaged across all depth fractions of the core sample to a depth of 150 cm.

CADMIUM IN ELIZABETH RIVER SEDIMENT BY STATION AND LOCATION



CHROMIUM IN ELIZABETH RIVER SEDIMENT BY STATION AND LOCATION

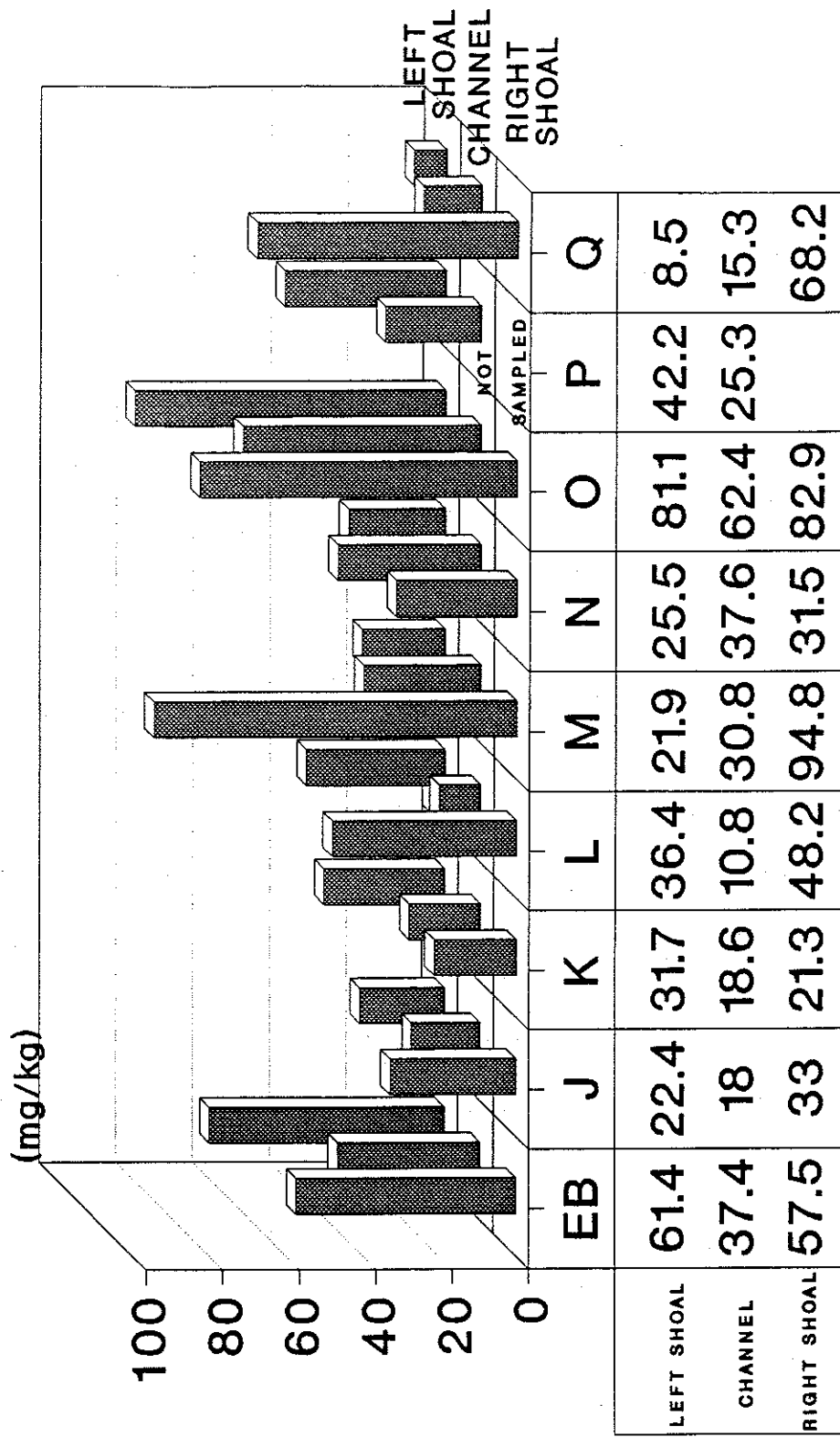


Figure 4. Copper concentrations in Elizabeth River sediments by site and transect location. Values represented by each bar are the concentrations averaged across all depth fractions of the core sample to a depth of 150 cm.

COPPER IN ELIZABETH RIVER SEDIMENT BY STATION AND LOCATION

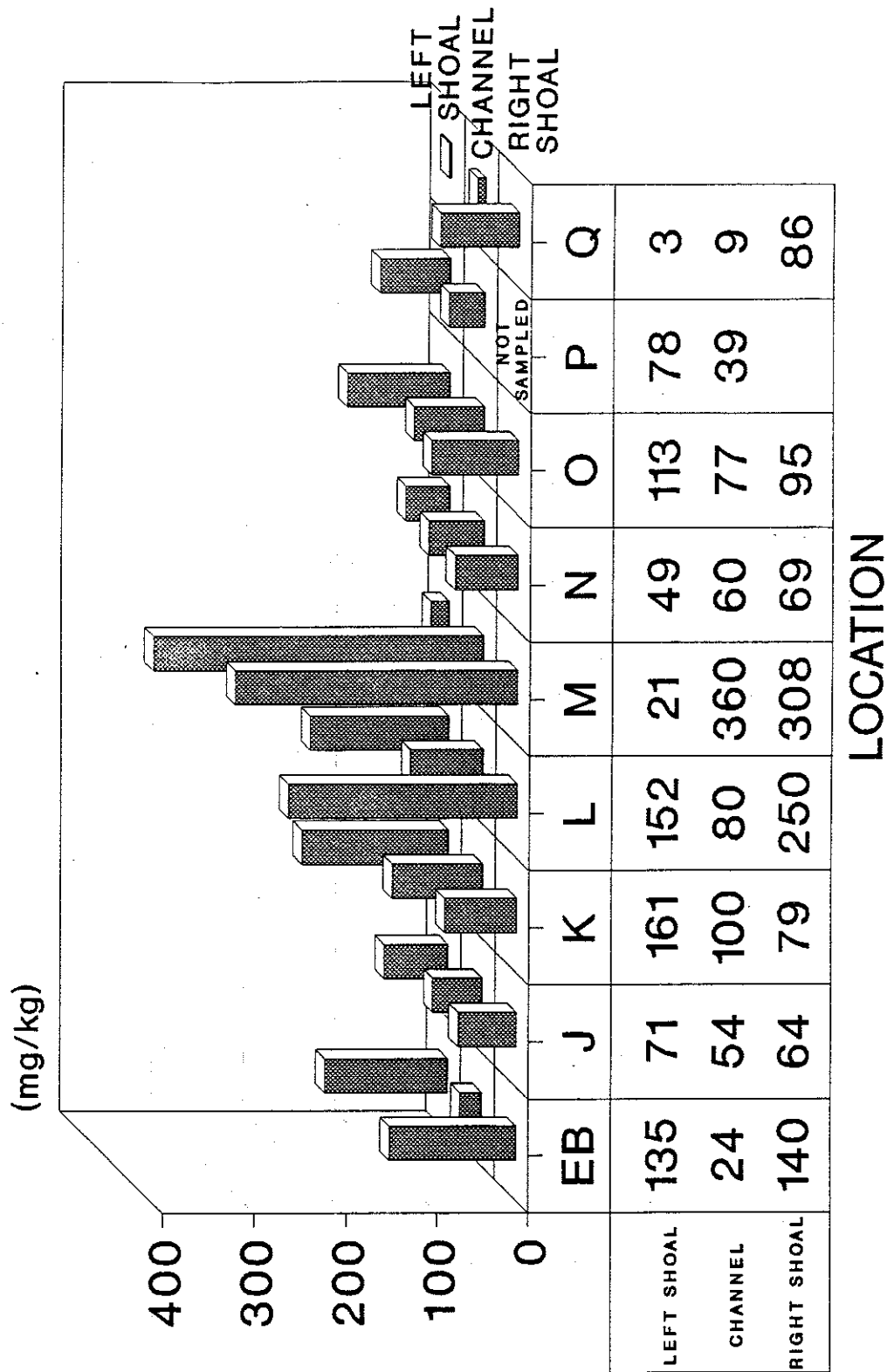


Figure 5. Iron concentrations in Elizabeth River sediments by site and transect location. Values represented by each bar are the concentrations averaged across all depth fractions of the core sample to a depth of 150 cm.

IRON IN ELIZABETH RIVER SEDIMENT BY STATION AND LOCATION

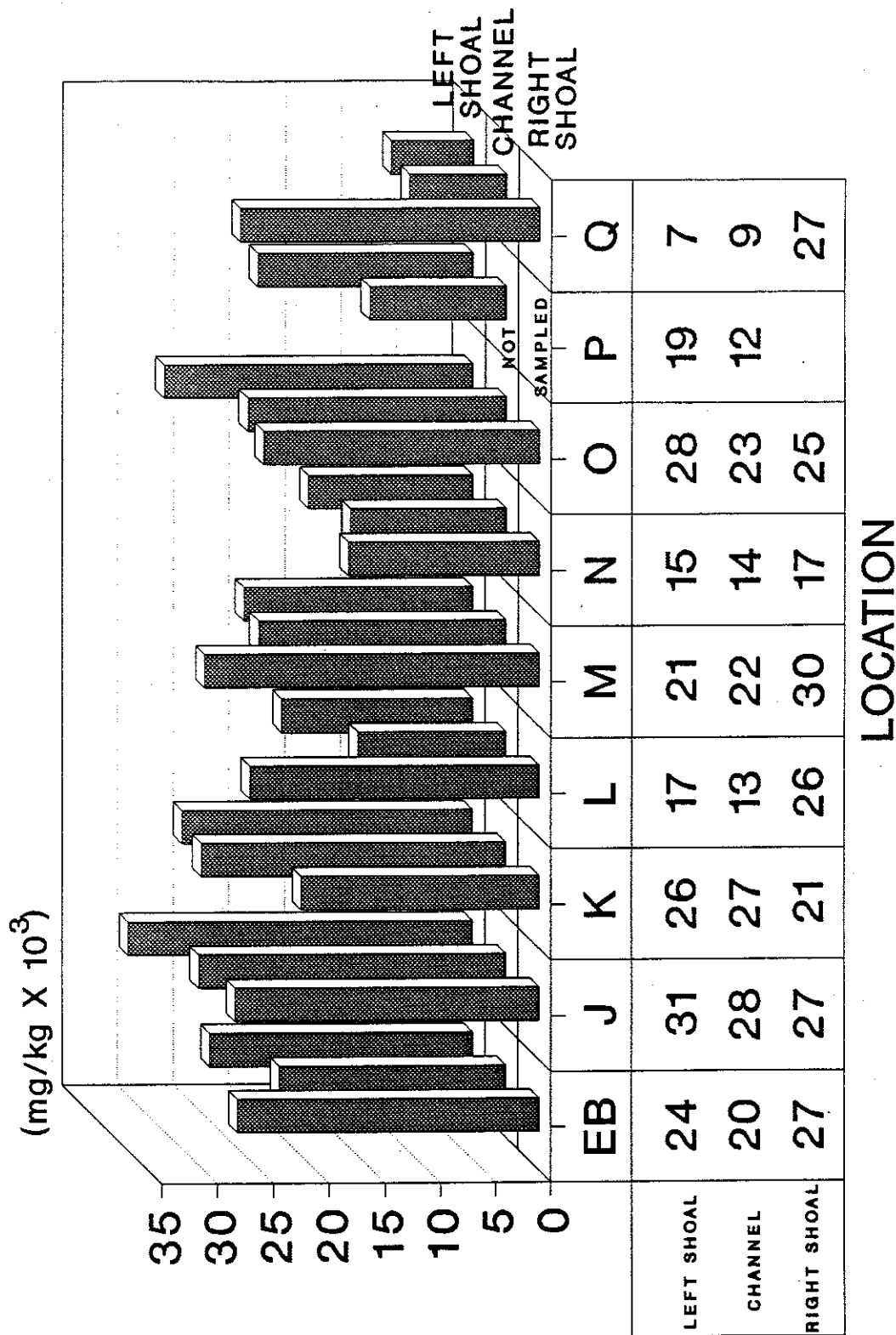
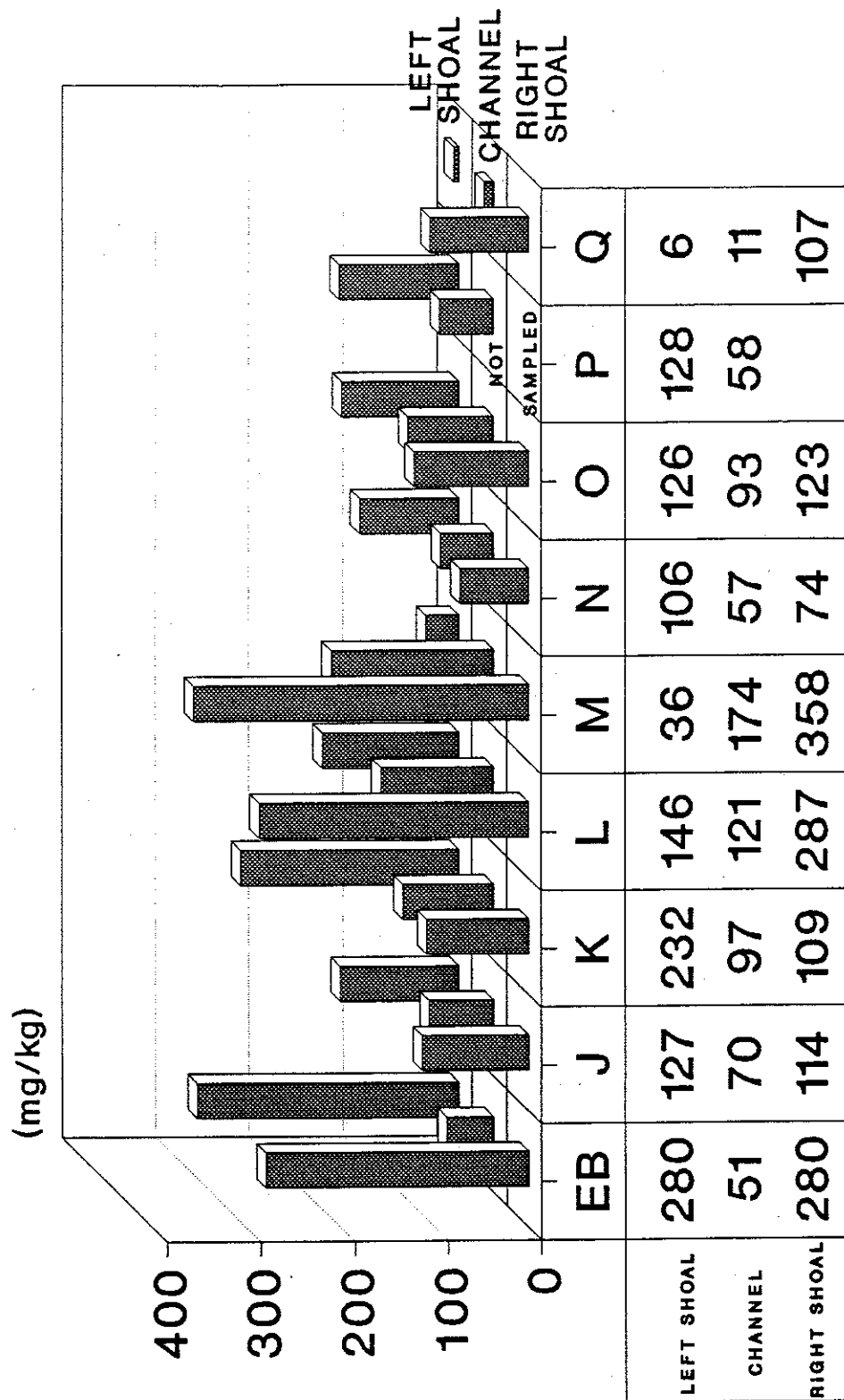


Figure 6. Lead concentrations in Elizabeth River sediments by site and transect location. Values represented by each bar are the concentrations averaged across all depth fractions of the core sample to a depth of 150 cm.

LEAD IN ELIZABETH RIVER SEDIMENT BY STATION AND LOCATION



LOCATION

Figure 7. Mercury concentrations in Elizabeth River sediments by site and transect location. Values represented by each bar are the concentrations averaged across all depth fractions of the core sample to a depth of 150 cm.

MERCURY IN ELIZABETH RIVER SEDIMENT BY STATION AND LOCATION

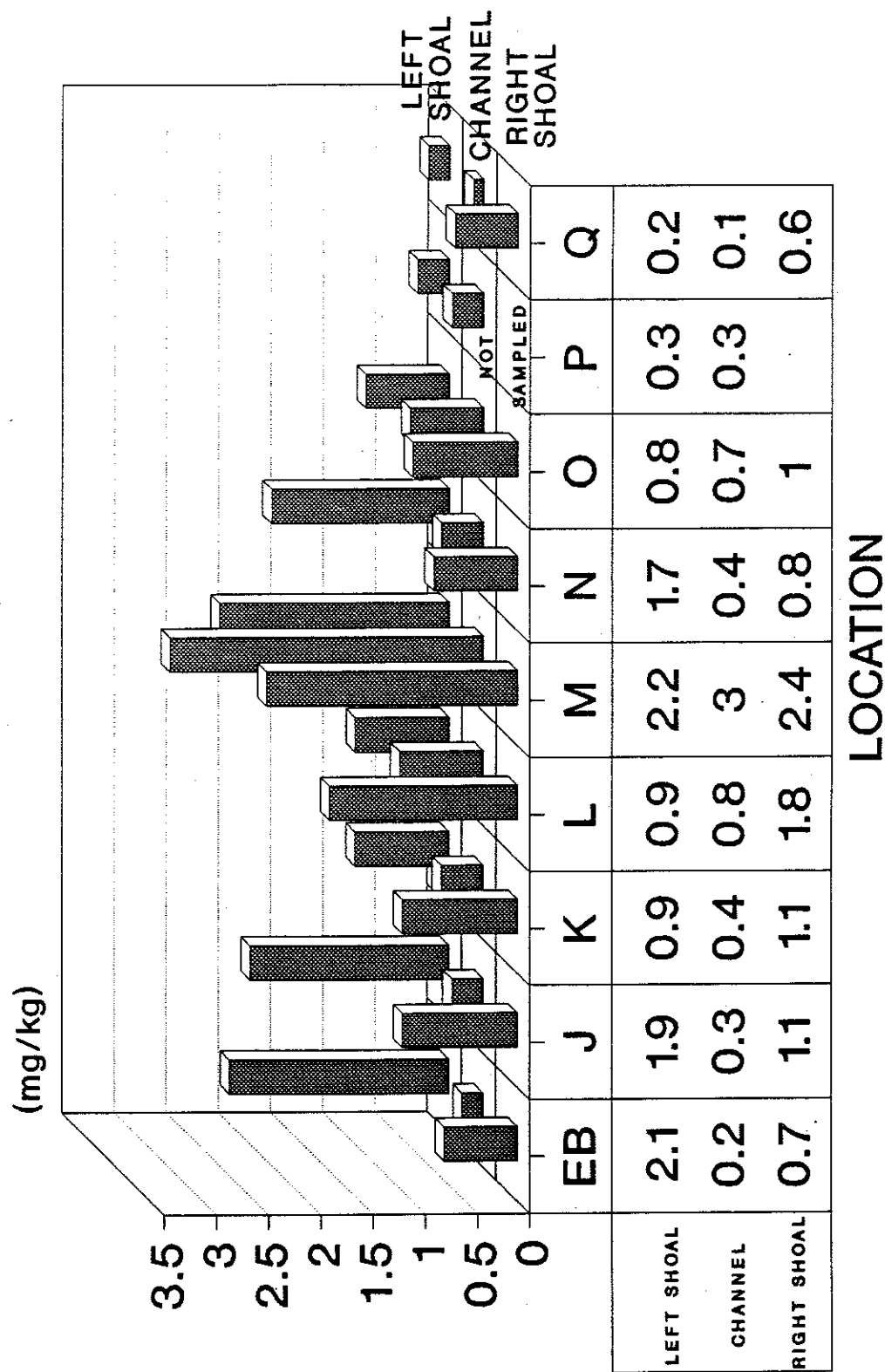


Figure 8. Nickel concentrations in Elizabeth River sediments by site and transect location. Values represented by each bar are the concentrations averaged across all depth fractions of the core sample to a depth of 150 cm.

NICKEL IN ELIZABETH RIVER SEDIMENT BY STATION AND LOCATION

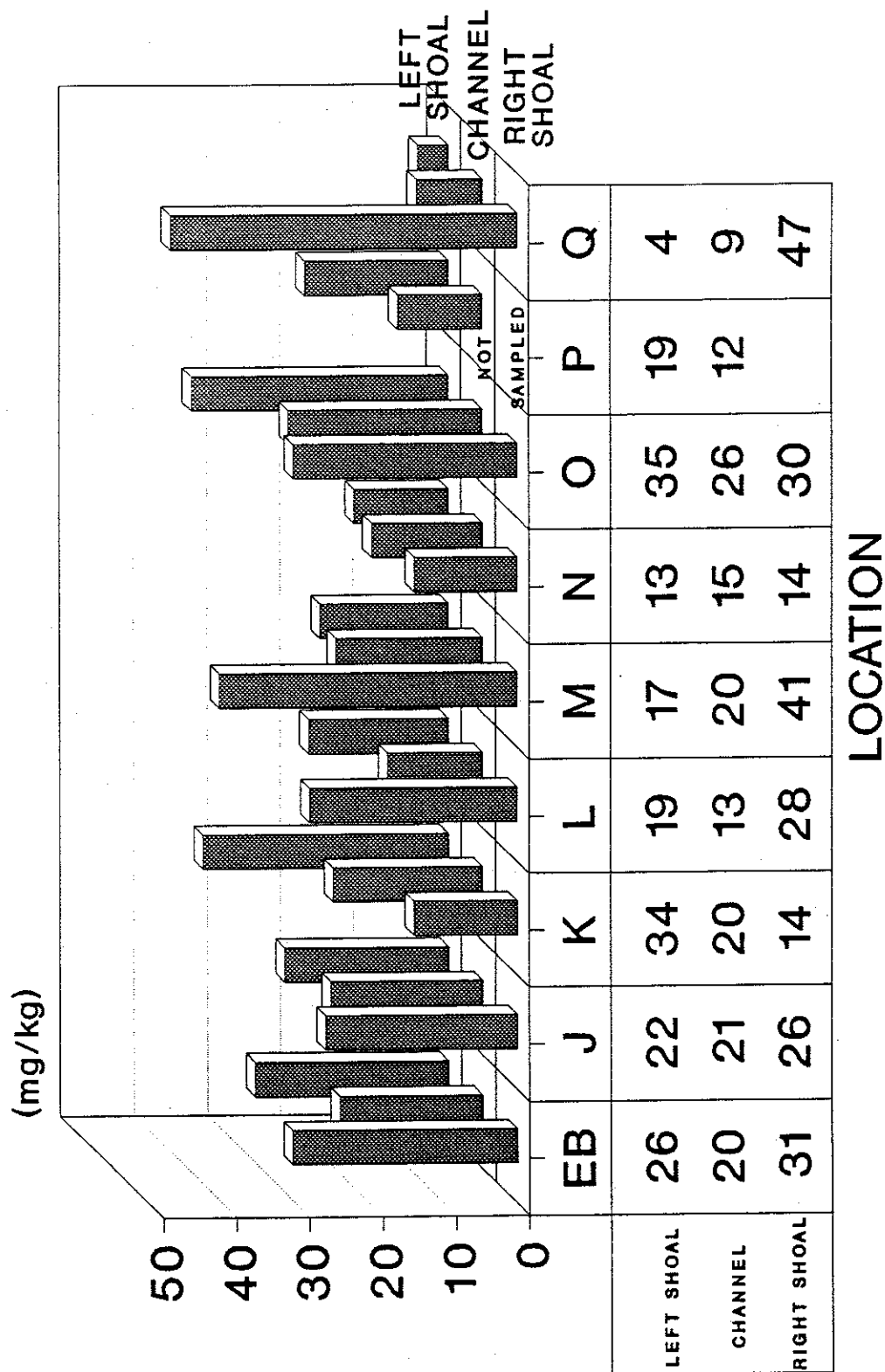


Figure 9. Selenium concentrations in Elizabeth River sediments by site and transect location. Values represented by each bar are the concentrations averaged across all depth fractions of the core sample to a depth of 150 cm.

SELENIUM IN ELIZABETH RIVER SEDIMENT BY STATION AND LOCATION

(mg/kg)

ALL BDL (<8.3)

LEFT
SHOAL
CHANNEL
RIGHT
SHOAL

0

EB	J	K	L	M	N	O	P	Q
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0		0

LEFT SHOAL
CHANNEL
RIGHT SHOAL

LOCATION

NOT
SAMPLED

Figure 10.

Silver concentrations in Elizabeth River sediments by site and transect location. Values represented by each bar are the concentrations averaged across all depth fractions of the core sample to a depth of 150 cm.

SILVER IN ELIZABETH RIVER SEDIMENT BY STATION AND LOCATION

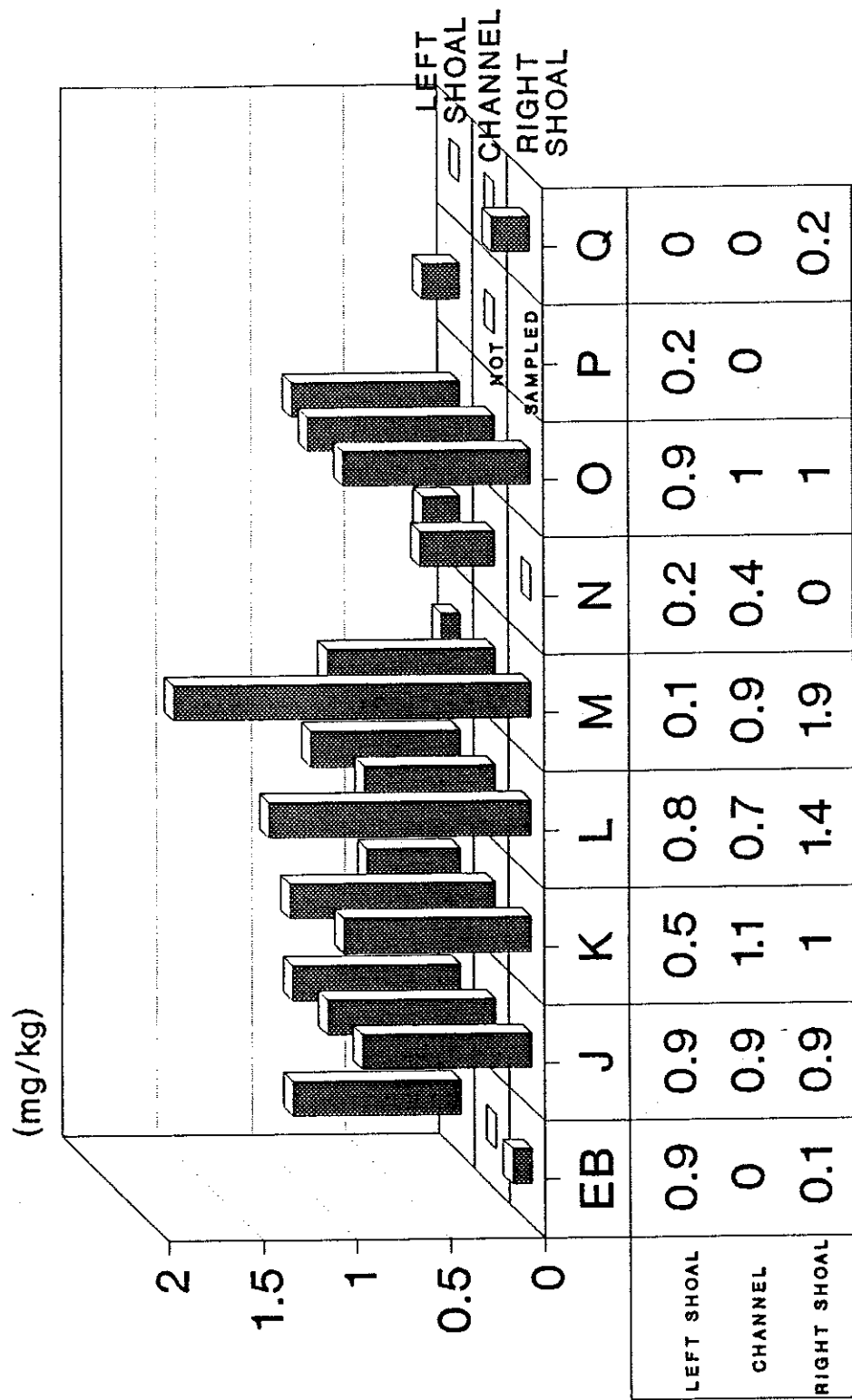
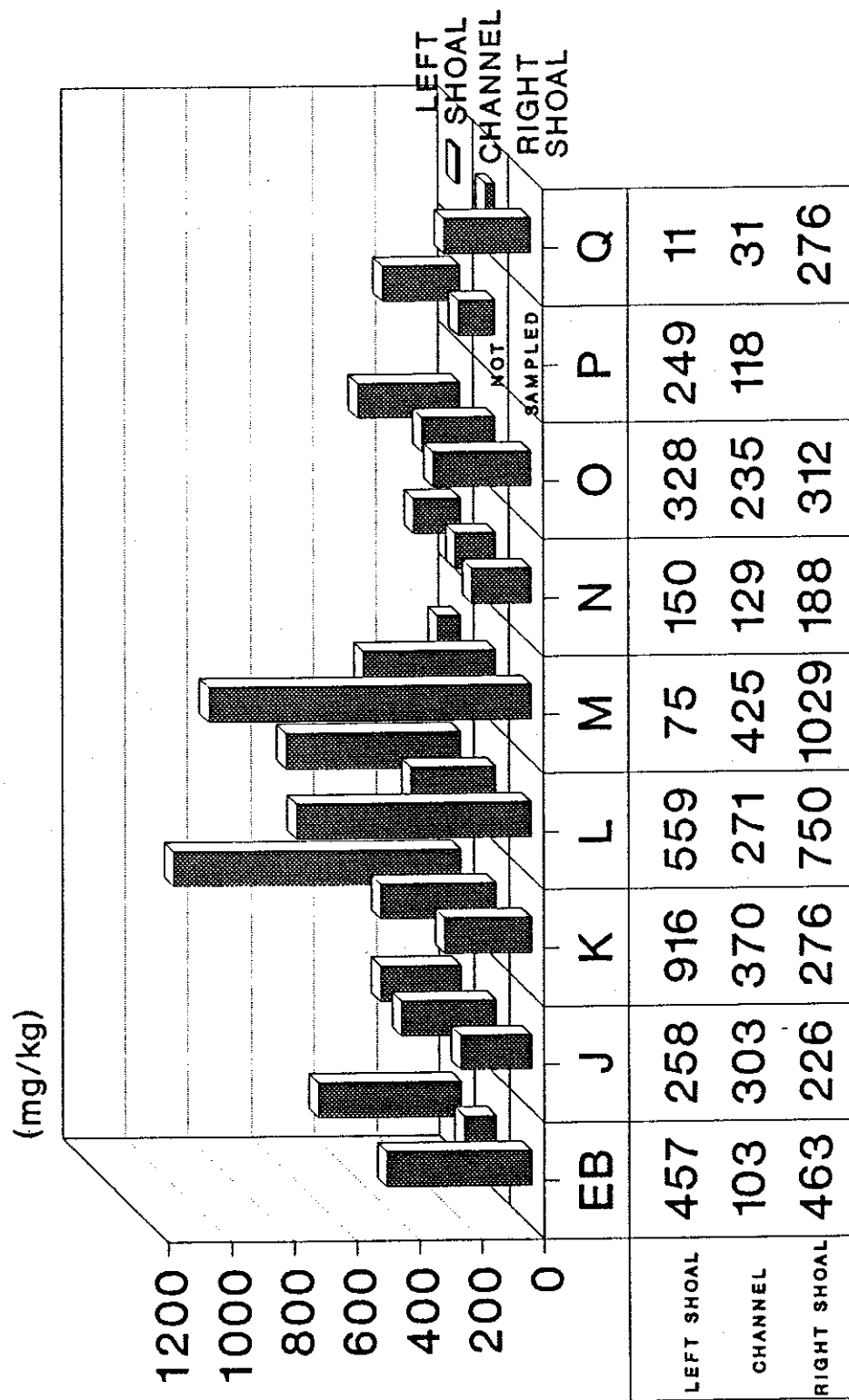


Figure 11. Zinc concentrations in Elizabeth River sediments by site and transect location. Values represented by each bar are the concentrations averaged across all depth fractions of the core sample to a depth of 150 cm.

ZINC IN ELIZABETH RIVER SEDIMENT BY STATION AND LOCATION



LOCATION

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Geographical and Depth Distribution Patterns by Metal

Cadmium

Shoals

Concentrations ranged from <0.5 mg/kg at several sites to 3.27 mg/kg at Site M (Fig. 12). The highest concentrations were found in sediments collected in the vicinity of shipyards on the Eastern and Southern Branches, and as was the case for many of the metals, the concentrations 1) decreased with distance from these industries and 2) were higher on the right shoal than on the left shoal (with a noticeable exception at Site EB, see Fig. 12). A similar pattern was noted by Johnson and Villa (1976) for samples collected in 1974 from the most industrialized section of the Southern Branch. Cadmium concentrations tended to increase with depth in the sediment and were almost always lowest in the 0-10 cm fraction at each station. This depth distribution pattern is in contrast to the 1974 study (Johnson and Villa, 1976), which reported cadmium concentrations in near surface sediments (5-15 cm deep) several factors greater than found throughout most of the River in the present study (in the upper 10 cm samples).

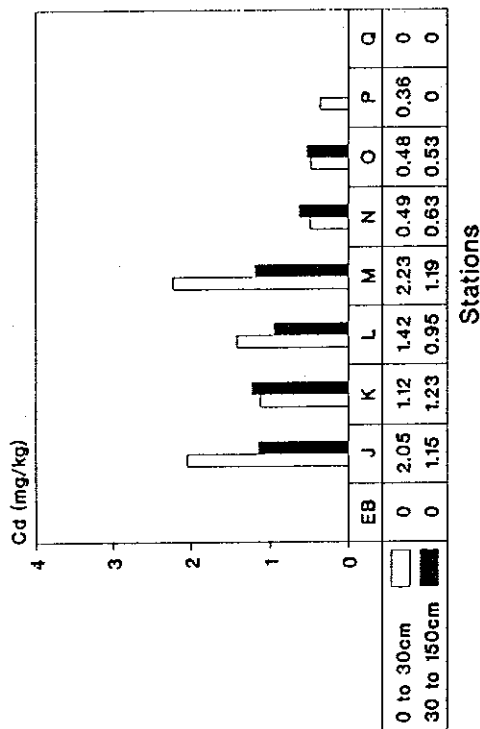
Channel

Concentrations ranged from <0.5 mg/kg at several sites to 2.23 mg/kg at Site M (Fig. 12). The highest cadmium values observed in the channel were in the vicinity of shipyards along the Southern Branch and at mainstem Site J. The low concentrations (i.e. near or below the detection level) observed at Sites N-Q in the Southern

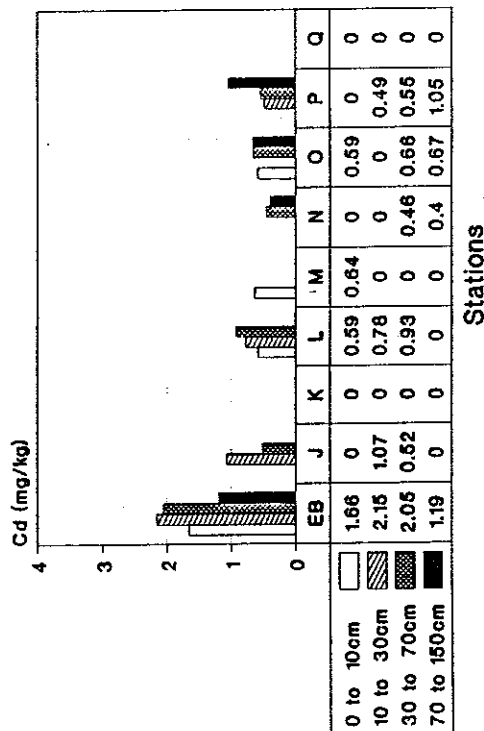
Figure 12.

Cadmium concentrations in Elizabeth River sediments by core sample depth interval, site and transect location. Zero indicates concentration below detection level (0.5 mg/kg).

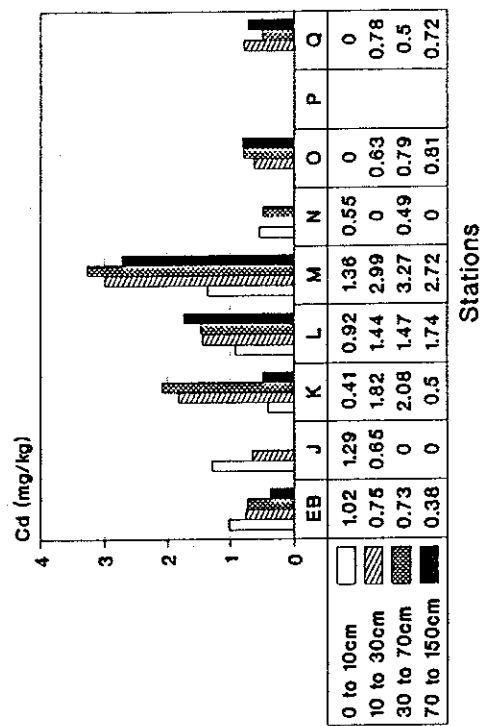
Cadmium in Sediments Elizabeth River (Channel)



Cadmium in Sediments Elizabeth River (L. Shoal)



Cadmium in Sediments Elizabeth River (R. Shoal)



Branch may be a reflection of the distance from possible sources of input of this metal into the River. However, the absence of detectable quantities of cadmium in channel samples from Site EB was somewhat surprising but may be due to a relatively recent dredging of sediments from this area.

Chromium

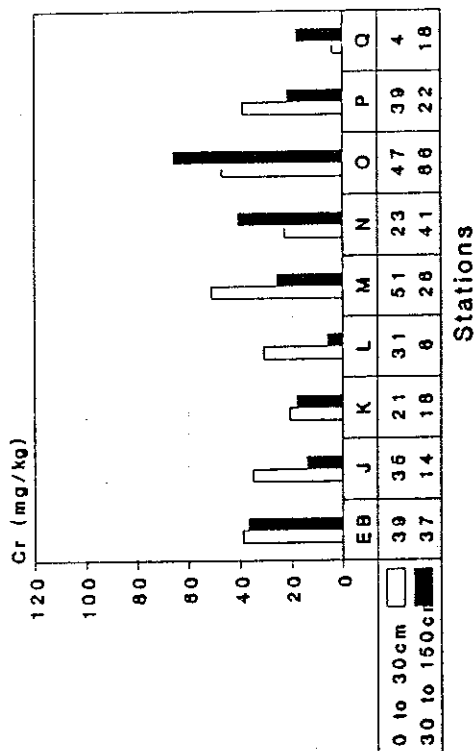
Shoals

Concentrations ranged from 3 mg/kg (Site K, 0-10cm; Site Q, 70-150 cm) to 104 mg/kg (Site M, 30-70 cm) (Fig. 13). The spatial pattern of chromium varied greatly, both in distribution with depth and geographically. In general, concentrations tended to increase with depth in the sediment, thus indicating that historical, rather than recent, inputs to the River were greater. Many of the higher chromium values were observed in the vicinity of shipyards. However, unlike most of the other metals, chromium was observed in equivalent or higher concentrations in sediments collected further upstream of Site M (i.e. Sites O-Q). Johnson and Villa (1976) reported similar patterns for 1974 collections, which confirm the contaminant loading from site L-Q. However, chromium values in all collections were at most two times greater than reported for the Chesapeake Bay and an order of magnitude less than average Baltimore Harbor concentrations (Johnson and Villa, 1976). Thus, chromium does not appear to represent a major problem in the Port.

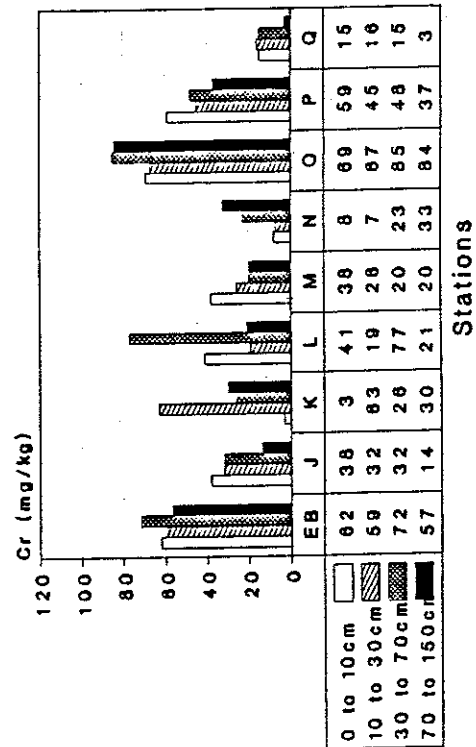
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Figure 13. Chromium concentrations in Elizabeth River sediments by core sample depth interval, site and transect location.

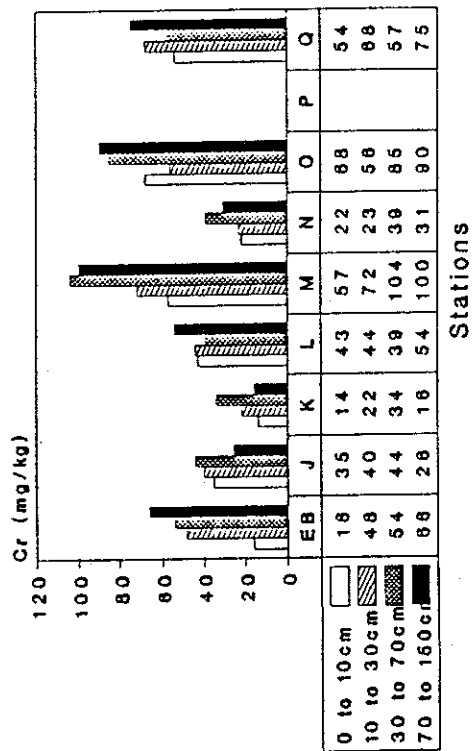
Chromium in Sediments Elizabeth River (Channel)



Chromium in Sediments Elizabeth River (L. Shoal)



Chromium in Sediments Elizabeth River (R. Shoal)



Channel

Concentrations ranged from 4 mg/kg (Site Q, 0-30 cm) to 66 mg/kg (Site O, 30-150 cm) (Fig. 13). The highest chromium values were observed in the 0-30 cm fractions at Sites EB, J-M, and P and in the lower 30-150 cm samples from Sites N, O and Q.

Copper

Shoals

Concentrations ranged from 1 mg/kg (Site Q, 70-150 cm) to 633 mg/kg (Site K, 10-30 cm) (Fig. 14). Copper concentrations were highest in the vicinity of the shipyards on the Eastern and Southern Branches (i.e. right shoal of Sites EB, L and M, and left shoal of Sites K and L) and were approximately the same throughout the rest of the study area. Johnson and Villa (1976) reported very similar spatial patterns for 1974 collections, but their highest concentrations were generally 100-200 mg/kg and only greatly exceeded 200 mg/kg for one site (395 mg/kg for site M).

Channel

Concentrations ranged from 3 mg/kg (Site Q, 0-30 cm) to 987 mg/kg (Site M, 0-30 cm) (Fig. 14). Near surface (0-30 cm) sediment concentrations regularly increased moving upstream from Site J to Site M. The concentration of copper in the Site M, 0-30 cm sample was 5-10 times greater than that observed in this fraction at other channel sites. These conditions suggest a recent and/or continuing source of copper contamination.

Iron

Shoals

Concentrations ranged from 5,460 mg/kg (Site Q, 70-150 cm) to 33,900 mg/kg (Site J, 10-30 cm) (Fig. 15). Iron concentrations were generally high throughout the River (but slightly higher in the lower reaches) and no consistent depth distribution pattern was observed. Similiar spatial patterns and concentrations were observed by Johnson and Villa (1976) in their 1974 near surface sediment (5-15 cm) collections.

Channel

Concentrations ranged from 4,780 mg/kg (Site Q, 0-30 cm) to 33,500 mg/kg (Site J, 0-30 cm) (Fig. 15). In general, iron was slightly more abundant throughout the more industrialized portions of the River (Sites EB, J-M) and was almost always found in greater concentrations in the upper 30 cm fractions than in the deeper channel sediments.

Lead

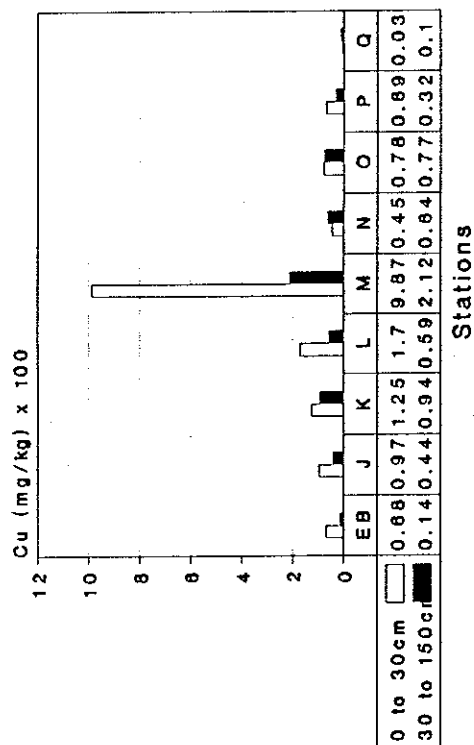
Shoals

Concentrations ranged from 3 mg/kg (Site Q, 70-150 cm) to 600 mg/kg (Site EB, 0-10 cm) (Fig. 16). Lead in right shoal sediments showed a pattern of increase from Site J to Site M and was considerably lower further upstream; lead in left shoal sediments showed no consistent pattern throughout the River except for

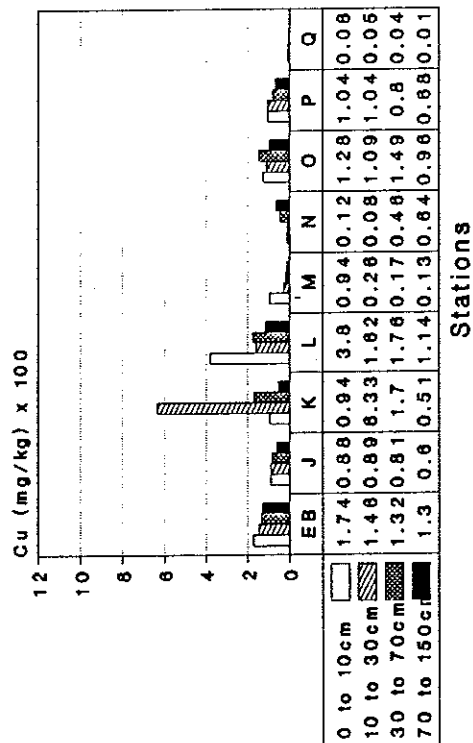
Figure 14.

Copper concentrations in Elizabeth River sediments by core sample depth interval, site and transect location. Note that concentrations plotted equal mg/kg X 100.

Copper in Sediments Elizabeth River (Channel)



Copper in Sediments Elizabeth River (L. Shoal)



Copper in Sediments Elizabeth River (R. Shoal)

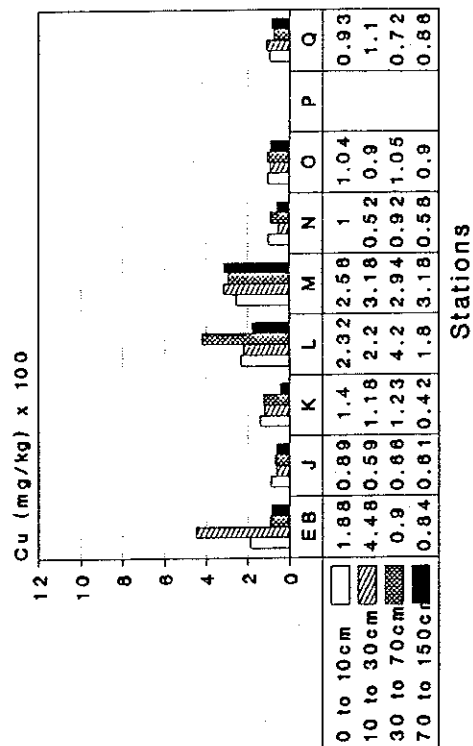
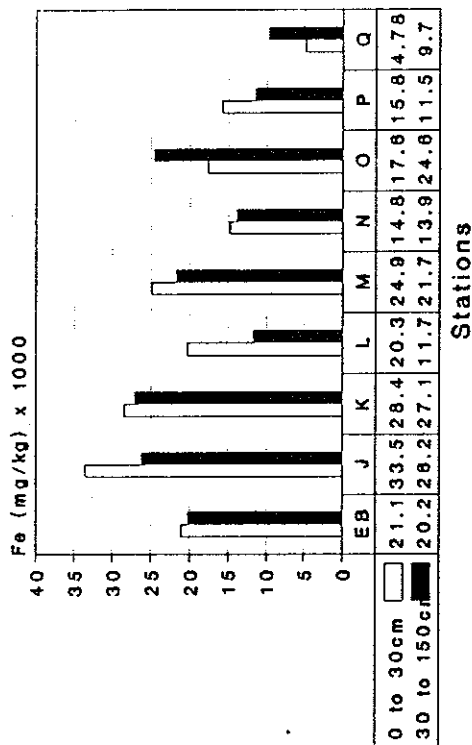


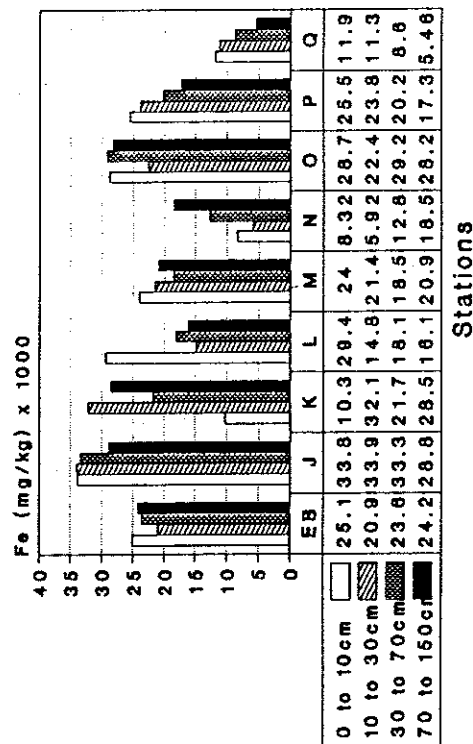
Figure 15.

Iron concentrations in Elizabeth River sediments by core sample depth interval, site and transect location. Note that concentrations plotted equal mg/kg X 1000.

Iron in Sediments Elizabeth River (Channel)



Iron in Sediments Elizabeth River (L. Shoal)



Iron in Sediments Elizabeth River (R. Shoal)

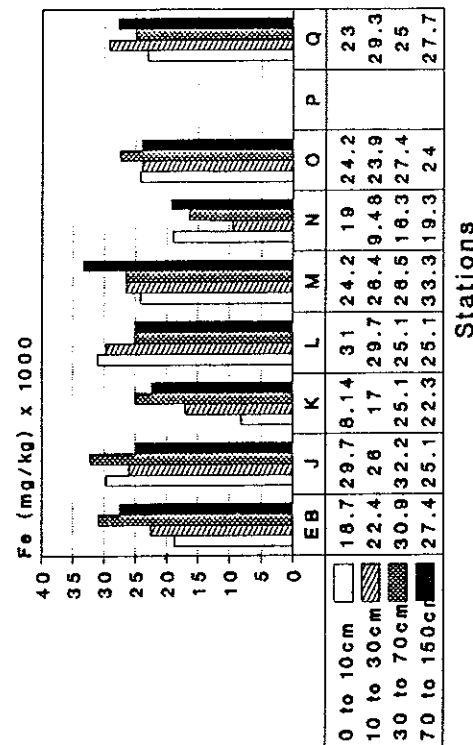
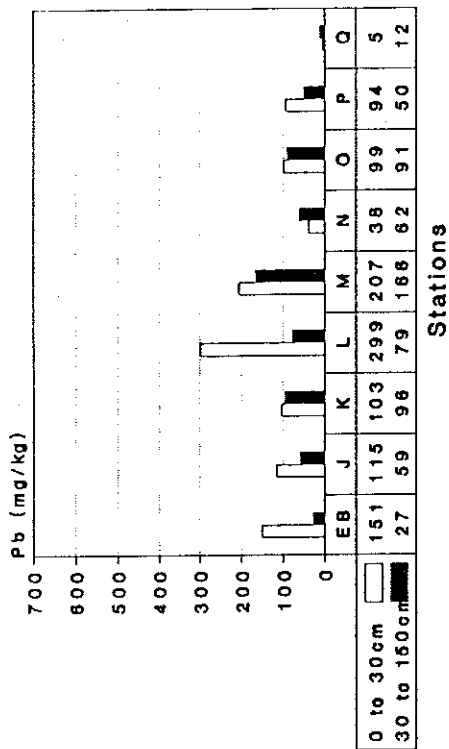
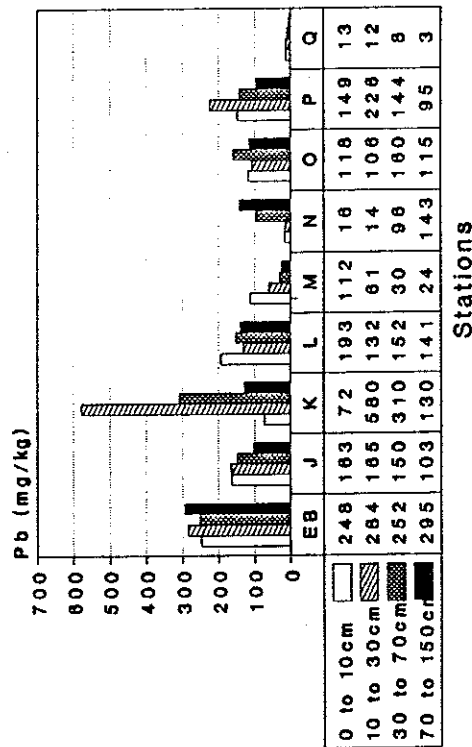


Figure 16. Lead concentrations in Elizabeth River sediments by
core sample depth interval, site and transect
location.

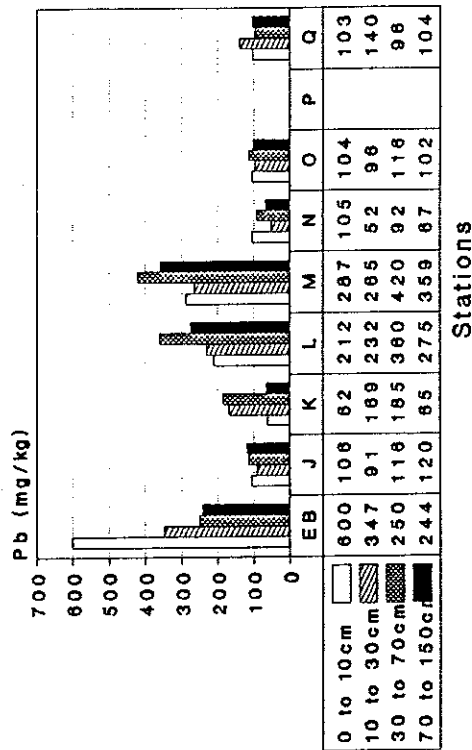
Lead in Sediments Elizabeth River (Channel)



Lead in Sediments Elizabeth River (L. Shoal)



Lead in Sediments Elizabeth River (R. Shoal)



noticeably higher concentrations at Sites EB and K (vicinity of shipyards). Lead was generally more abundant in the deeper fractions of shoal samples compared to the upper 10 cm of sediment. However, an extremely obvious exception to this pattern was noted at Site EB, where the highest lead concentration observed in the study was seen in the 0-10 cm sample from the right shoal. Johnson and Villa (1976) found the highest lead values in the vicinity of Site EB and in the right shoal areas adjacent to Sites L and M, which tends to confirm the patterns observed in the present study.

Channel

Concentrations ranged from 5 mg/kg (Site Q, 0-30 cm) to 299 mg/kg (Site L, 0-30 cm) (Fig. 16). Lead concentrations were higher in the vicinity of shipyards and were almost always higher in the top 30 cm fractions than in the deeper sediments.

Mercury

Shoals

Concentrations ranged from 0.09 mg/kg (Site K, 0-10 cm) to 3.37 mg/kg (Site M, 70-150 cm) (Fig. 17). On the right shoal, mercury concentrations generally increased with increasing depth in the sediment moving up the Southern Branch from Site J to Site M, and with the exception of a high value in the surface sediments (0-10 cm fraction) at Site N (adjacent to the "mothball fleet"), the concentrations were noticeably lower at sites further upstream.

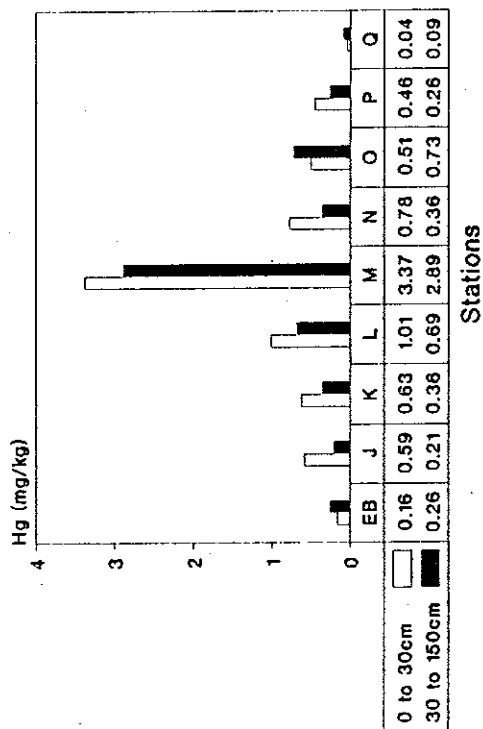
On the left shoal the highest concentrations were observed at Sites EB, M and N in the deepest (70-150 cm) samples collected, while at Site J high concentrations were found in all depth fractions. Mercury tended to occur at greater concentrations below 10 cm in the sediment which suggests that deposition may have been historical. However, in two 0-10 cm samples (Sites J, left shoal and N, right shoal) the mercury values were at or above 2 mg/kg. When it was discovered that some sediments had mercury concentrations in excess of 2 ppm, extra precautions were taken to minimize the possible health risks to technicians handling the samples. Johnson and Villa (1976) reported their highest mercury value (1.49 mg/kg) in the near surface (5-15 cm) sediments from the left shoal of an area located between Sites M and N. Thus it appears that the 1974 distribution pattern of mercury in this region of the River is comparable to that observed in the near surface samples (10-30 samples) of the present study. Johnson and Villa (1976) also reported elemental mercury concentrations (>0.3 ppm) at many of the other sites in the Southern and Eastern Branches.

Channel

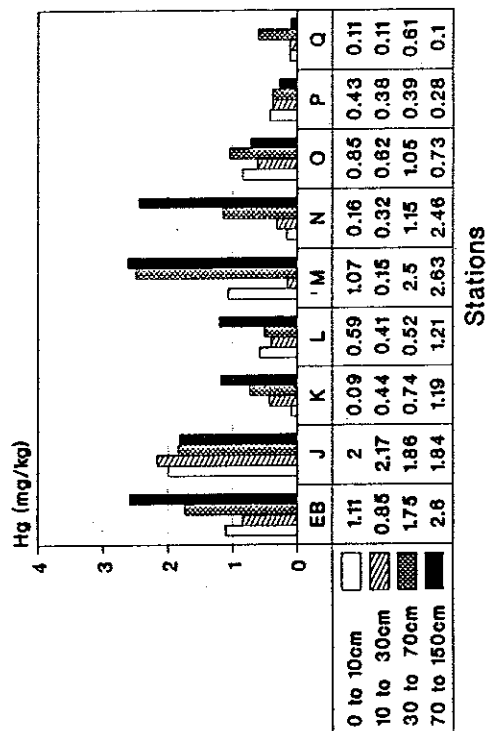
Concentrations ranged from 0.04 mg/kg (Site Q, 0-30 cm) to 3.37 mg/kg (Site M, 0-30 cm) (Fig. 17). With the exception of samples from at Sites L and M, mercury concentrations in channel sediments were less than 1.0 mg/kg throughout the study area.

Figure 17. Mercury concentrations in Elizabeth River sediments by core sample depth interval, site and transect location.

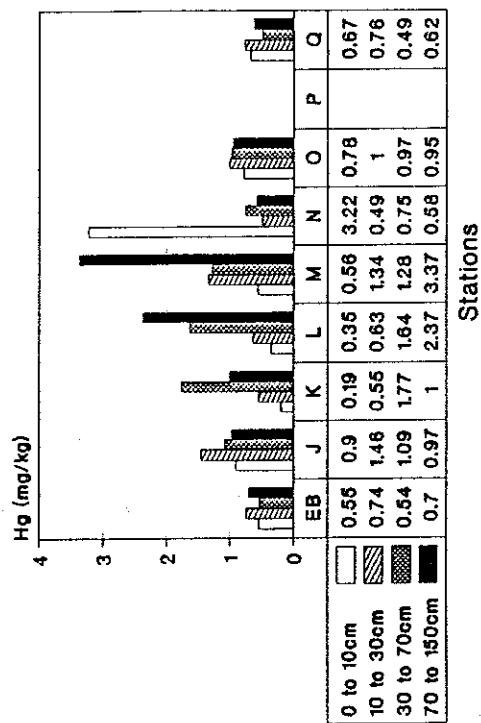
Mercury in Sediments Elizabeth River (Channel)



Mercury in Sediments Elizabeth River (L. Shoal)



Mercury in Sediments Elizabeth River (R. Shoal)



Nickel

Shoals

Concentrations ranged from 2 mg/kg (Site Q, 70-150 cm) to 136 mg/kg (Site M, 0-10 cm) (Fig. 18). Nickel concentrations varied little over the study area except for higher values observed in the Site M, 0-10 cm sample and in the Site K, 10-30 cm fraction. Since no obvious depth distribution patterns were noted, and nickel seems to be evenly distributed in each sediment fraction, a continuing source (natural or human origin) may be indicated.

Channel

Concentrations ranged from 5 mg/kg (Site Q, 0-30 cm) to 28 mg/kg (Site J, 0-30 cm; Site O, 30-150 cm) (Fig. 18). No significant spatial patterns were observed for nickel in channel sediments.

Selenium

The concentration of selenium was BDL (<8.3 mg/kg) in all sediment samples collected from the shoals and channel (Fig. 19).

Silver

Shoals

Concentrations ranged from <0.5 mg/kg (BDL) in several samples to 2.15 mg/kg (Site M, 70-150 cm) (Fig. 20). On both shoals, silver concentrations were higher in sediments collected along the

more industrialized portions of the River (primarily Sites J-M). This metal was generally more abundant in the >10 cm fractions than in the surface sediments, although one of the higher values observed was in the 0-10 cm sample of Site J (right shoal). Of particular interest is the disjunct distributional pattern of silver, i.e. the near absence of this metal at site N and its reoccurrence in relatively high concentrations at Sites O and P.

Channel

Concentrations ranged from <0.5 mg/kg (several samples) to 2.2 mg/kg (Site O, 0-30 cm) (Fig. 20). With only one exception (Site N), silver concentrations were higher in the upper 30 cm of channel sediments than in the deeper fraction. The values were near detection levels or BDL for samples collected at Sites EB, P and Q.

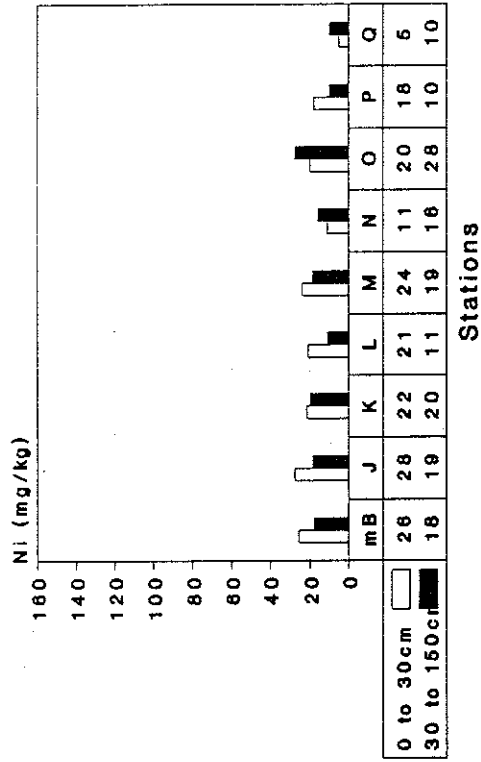
Zinc

Shoals

Concentrations ranged from 6 mg/kg (Site Q, 70-150 cm) to 4,220 mg/kg (Site K, 10-30 cm) (Fig. 21). Concentrations of zinc were approximately the same on both shoals of the River, although the highest values were observed in the vicinity of major shipyards. No obvious depth distribution pattern was noted except for higher concentrations at two sites (Site K, 10-30 cm; Site L, 0-10 cm). Johnson and Villa (1976) reported similar patterns for sediments collected in 1974 in 5 -15 cm-deep samples from the same

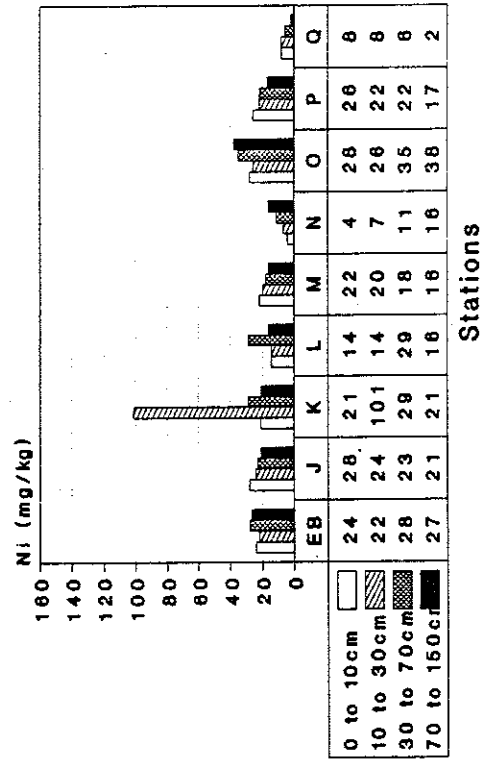
Figure 18. Nickel concentrations in Elizabeth River sediments by core sample depth interval, site and transect location.

Nickel in Sediments Elizabeth River (Channel)



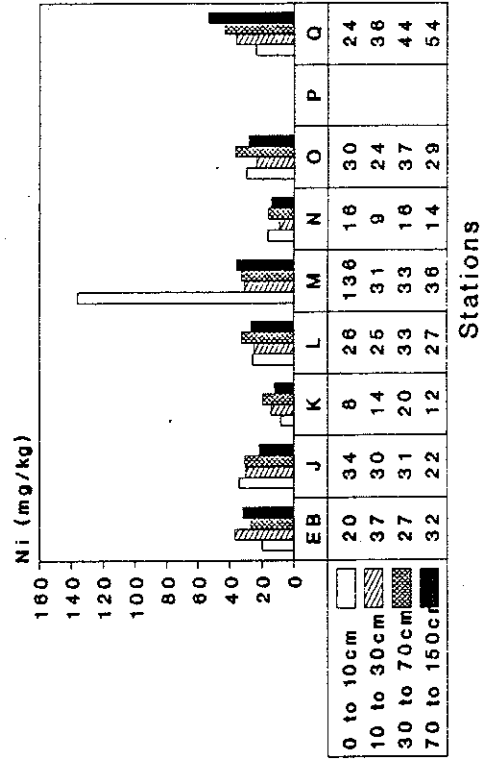
Stations

Nickel in Sediments Elizabeth River (L. Shoal)



Stations

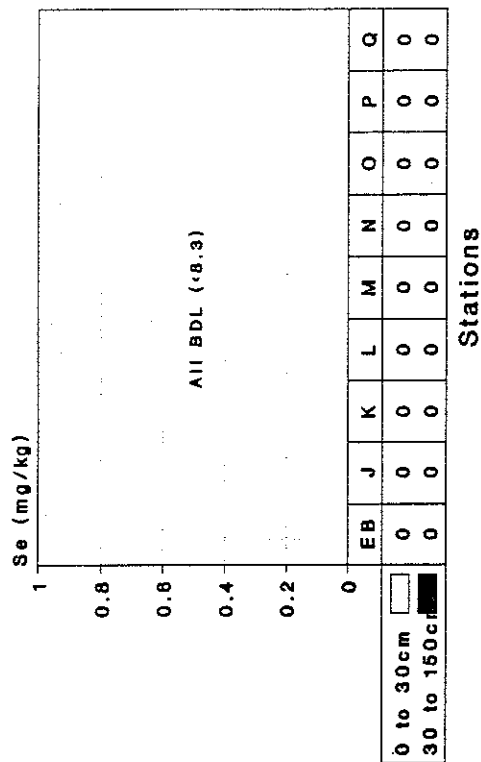
Nickel in Sediments Elizabeth River (R. Shoal)



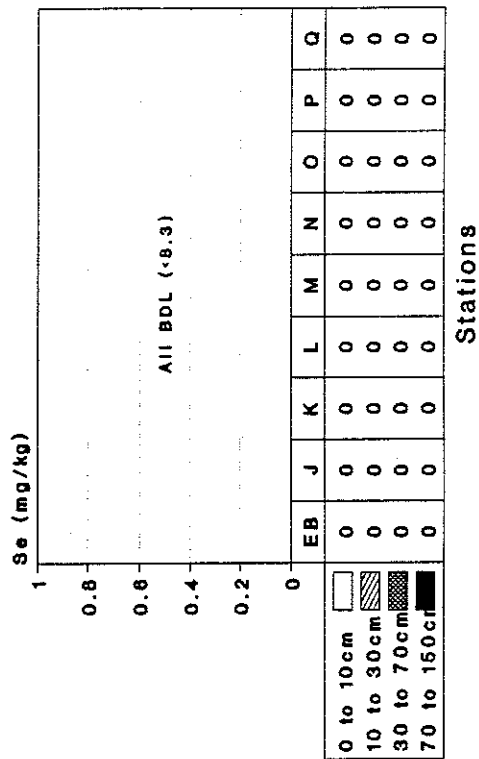
Stations

Figure 19. Selenium concentrations in Elizabeth River sediments by core sample depth interval, site and transect location.

Selenium in Sediments Elizabeth River (Channel)



Selenium in Sediments Elizabeth River (L. Shoal)



Selenium in Sediments Elizabeth River (R. Shoal)

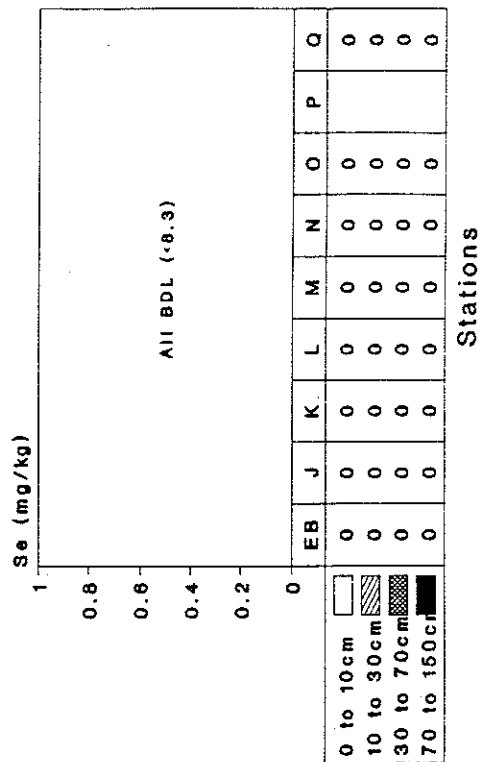
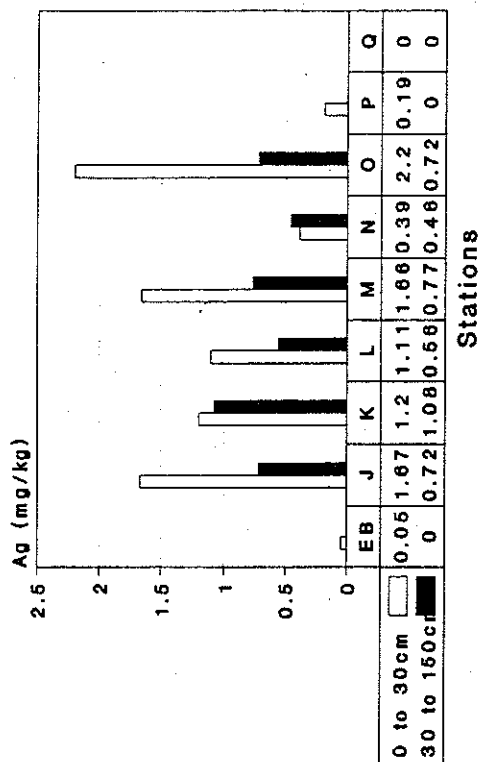


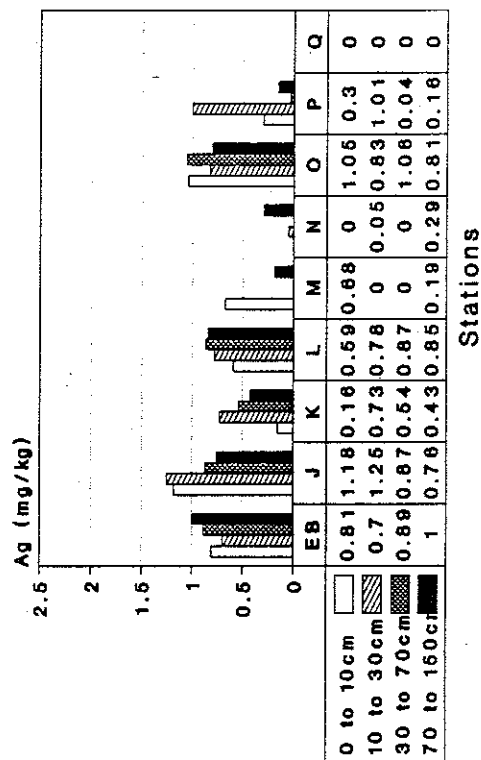
Figure 20.

Silver concentrations in Elizabeth River sediments by core sample depth interval, site and transect location.

Silver in Sediments Elizabeth River (Channel)



Silver in Sediments Elizabeth River (L. Shoal)



Silver in Sediments Elizabeth River (R. Shoal)

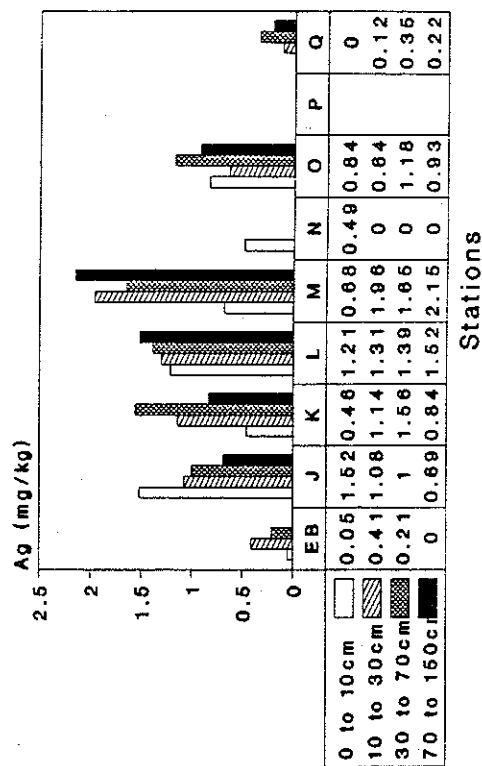
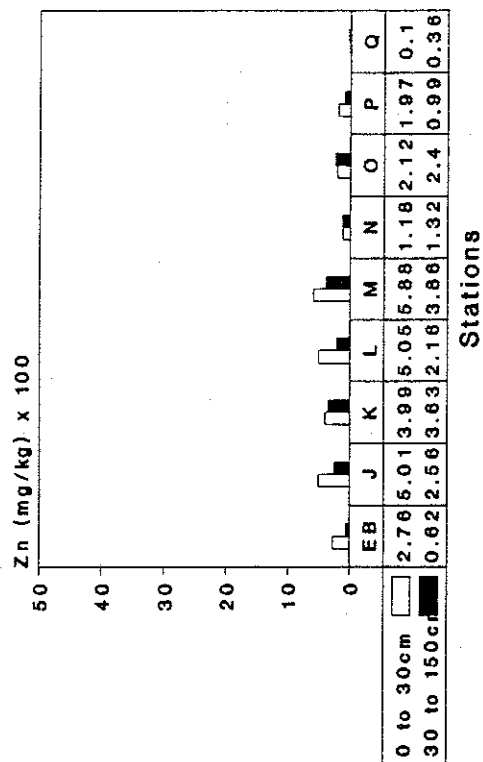


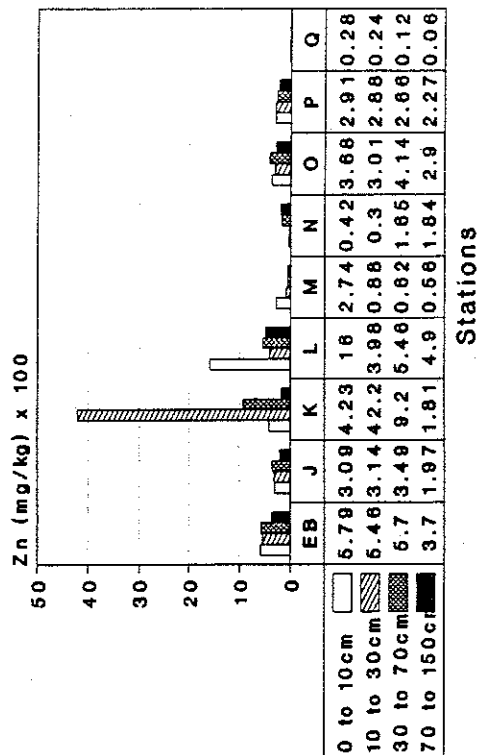
Figure 21.

Zinc concentrations in Elizabeth River sediments by core sample depth interval, site and transect location. Note that concentrations plotted equal $\text{mg/kg} \times 100$.

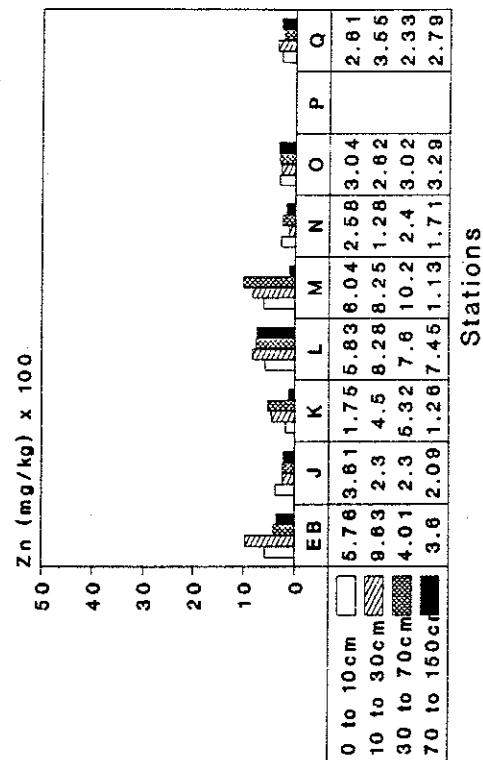
Zinc in Sediments Elizabeth River (Channel)



Zinc in Sediments Elizabeth River (L. Shoal)



Zinc in Sediments Elizabeth River (R. Shoal)



relative areas. Zinc concentrations were approximately the same for most locations (especially sites L and M right shoal), except for site K (4220 kg/mg), a value which greatly exceeded the Johnson and Villa (1976) study.

Channel

Concentrations ranged from 10 mg/kg (Site Q, 0-30 cm) to 588 mg/kg (Site M, 30-70 cm) (Fig. 21). Zinc concentrations in channel sediments from the Eastern Branch, mainstem and lower half of the Southern Branch (Sites K-M) were generally higher in the upper 30 cm samples than in the 30-150 cm samples.

ORGANIC CONTAMINANTS

General Comments

This section of the report details the spatial trends of organic contaminants in the sediments of the Elizabeth River System. These spatial trends will be discussed by: 1) the upstream/downstream patterns, by site, 2) the across river transects at each site, and 3) with depth for each transect sample. In order to better evaluate these trends, the raw organics data presented in Appendix D have been manipulated in such a way as to produce a limited number of graphs which contain information to evaluate the spatial trends. In order to simplify the complex matrix of contaminants determined during this project, the results have been combined for trend review purposes into the following three summary categories:

- 1) Total polynuclear aromatic hydrocarbons (PNAs) -
which includes the sum of all the PNAs detected as presented in Table 4.
- 2) Total phthalates- which includes the sum of all the phthalates detected as presented in Table 5.
- 3) Other miscellaneous, but significant, contaminants as presented in Table 6.

Each of these categories will be discussed in reference to the entire region of the Elizabeth River System evaluated during this project, as well as to each of the transects of the nine sites. When appropriate, we include mention of the types of land use in

Table 4. List of polynuclear aromatic hydrocarbons detected in Elizabeth River sediments. Note: all of these compounds are EPA "priority pollutants".

Acenaphthalene
Acenaphthene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene
Chrysene
Dibenzo(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

Table 5. List of phthalates detected in Elizabeth River sediments. Note: all of these compounds are "priority pollutants".

Bis(2-ethylhexylphthalate
Butylbenzylphthalate
Diethylphthalate
Di-n-butylphthalate
Di-n-octylphthalate

Table 6. List of miscellaneous organic compounds detected in Elizabeth River sediments. Asterisk denotes "priority pollutants".

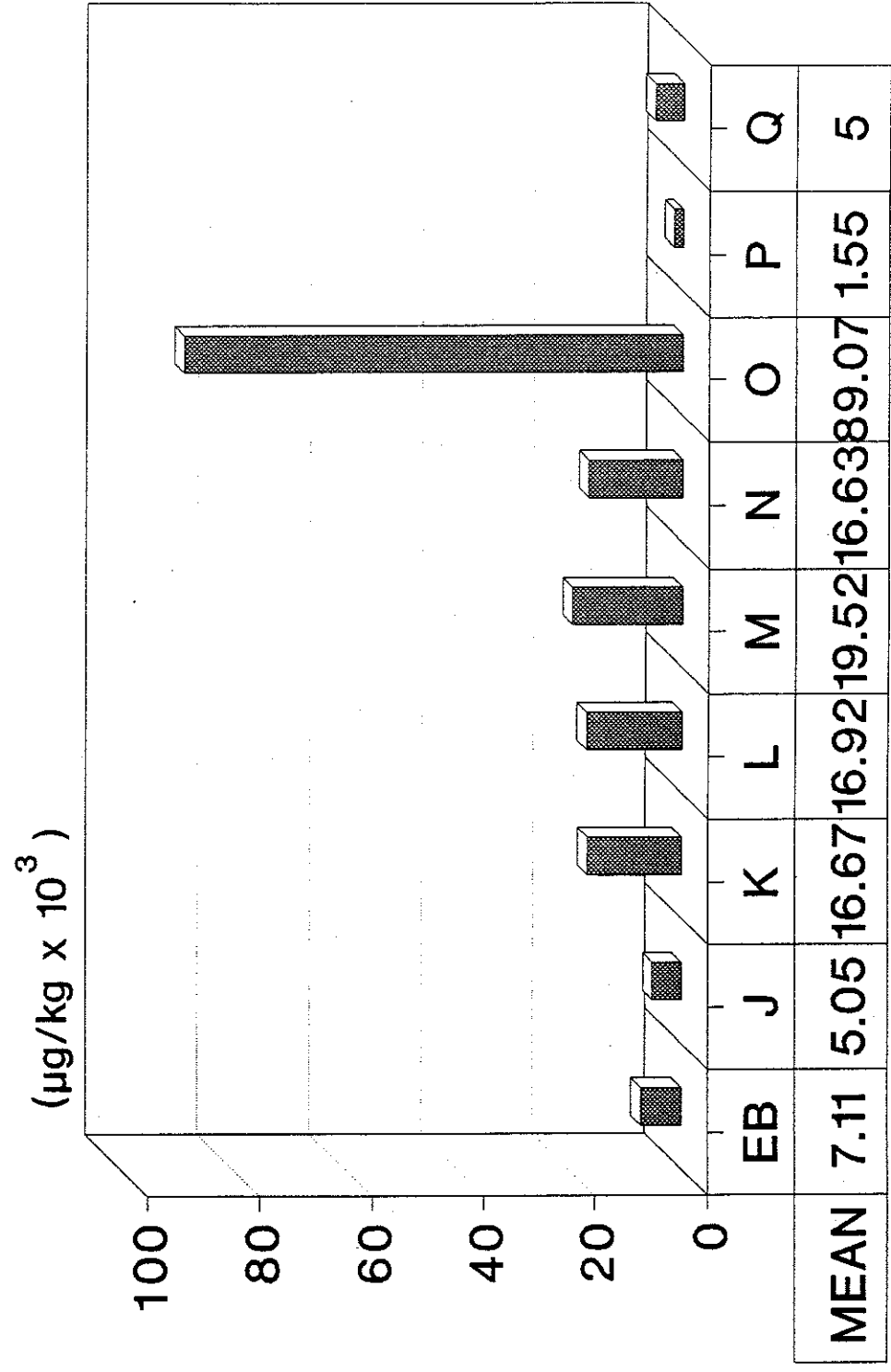
Benzoic acid
Dibenzofuran
*1,2-Dichlorobenzene
*1,3-Dichlorobenzene
*1,4-Dichlorobenzene
2-Methylnaphthalene
*n-Nitrosodiphenylamine
*Pentachlorophenol
*Phenol
*2,4,6-Trichlorophenol
*2,4-Dimethylphenol

relation to each of these sites in order to create an overall picture of the possible types of land use activities responsible for introducing contaminants into the Elizabeth River sediments.

Upon review of the raw data graphs presented in Appendix D, and the summary graphs (Figs. 22 and 23) presented throughout this section, the following points should be kept in mind. First, when a concentration is listed as "0" it actually represents a value that is below the detection limits (BDL) presented in Table 7. Second, the values illustrated in all organic contaminant graphs are reported using three (summary graphs) or four (raw data graphs) significant digits. In some cases, however, there may be fewer digits reported. This is due to the inability of the computer software used to generate these graphs to recognize trailing zeros. For example, if a compound has an input concentration of "1.260", the computer will generate a graph and list the value in the data table as "1.26". This does not affect the concentrations of the compounds or their graphical appearance, but only the appearance of the concentrations as listed in the data tables. Third, when trend generalizations involve the inclusion of the shoal (left and/or right) data, site P data are not included due to the exclusion of these samples from the original sampling design. Only upon discussing channel composite concentrations are site P data considered. Last, all concentrations reported in the graphs are in $\mu\text{g/kg}$ (often multiplied by 1000) dry sample weight or parts per billion (ppb). This method of presentation, rather than mg/kg (parts per million), was used to keep the data concentrations

Figure 22. Total average concentrations of polynuclear aromatic hydrocarbons (PNAs) by site.

TOTAL PNAS IN ELIZABETH RIVER SEDIMENT MEANS BY STATION



STATION

Figure 23. Total average concentrations of phthalates by site.

TOTAL PHTHALATES IN ELIZABETH RIVER SEDIMENTS

BY STATION

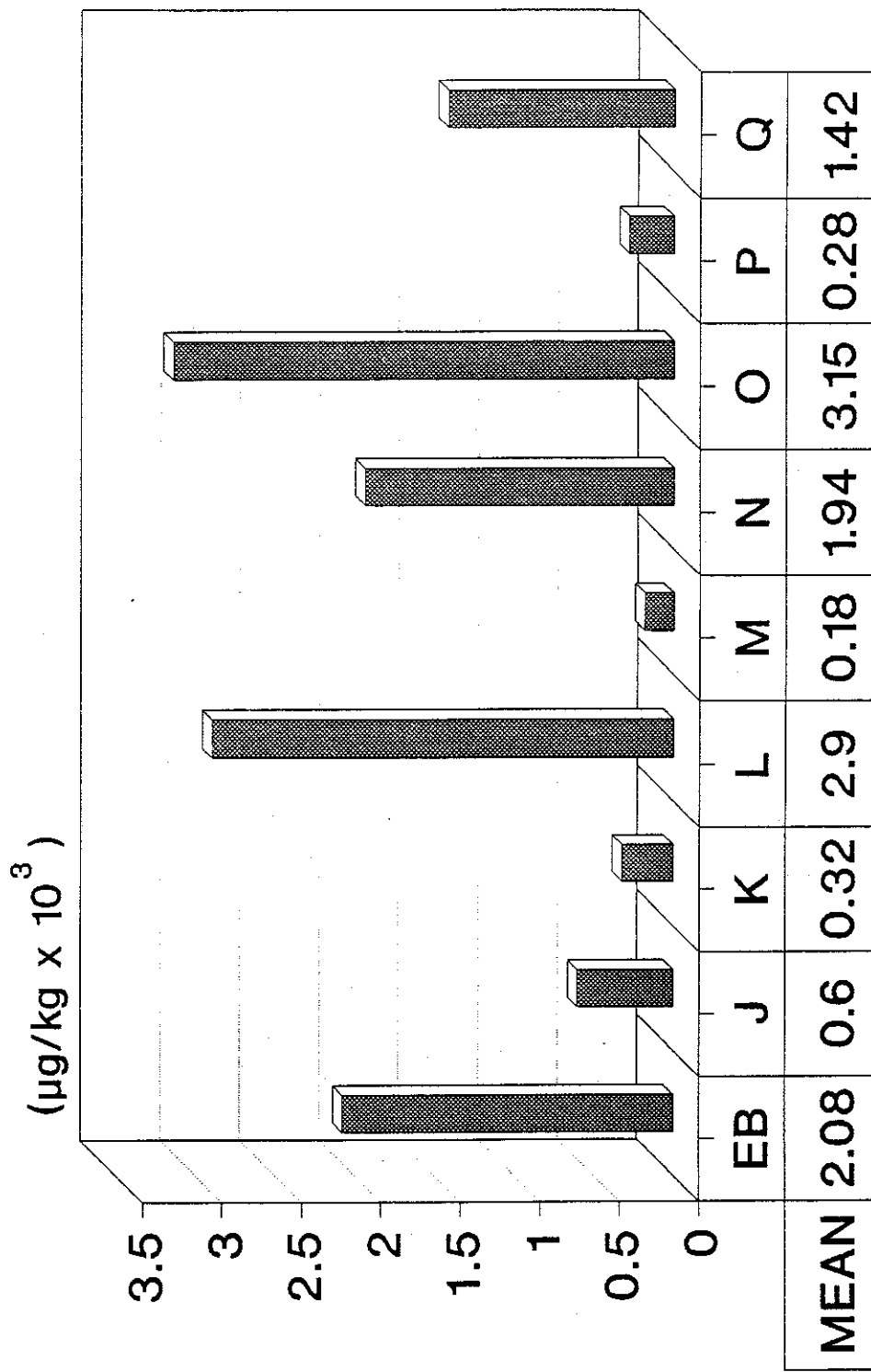


Table 7. List of all organic compounds analyzed and their corresponding detection limits.

<u>COMPOUND</u>	<u>DETECTION LIMIT ($\mu\text{g/kg}$)</u>
Phenol	25
Bis(2-chloroethyl) ether	25
2-Chlorophenol	25
1,2-Dichlorobenzene	25
1,3-Dichlorobenzene	25
1,4-Dichlorobenzene	25
Bis(2-chloroisopropyl) ether	25
N-Nitroso-di-n-propylamine	25
Hexachloroethane	25
Nitrobenzene	25
Isophorone	25
2-Nitrophenol	25
2,4-Dimethylphenol	25
Bis(2-chloroethoxy) methane	25
2,4-Dichlorophenol	25
1,2,4-Trichlorobenzene	25
Naphthalene	25
Hexachlorobutadiene	25
4-Chloro-3-methylphenol	50
Hexachlorocyclopentadiene	25
2,4,6-Trichlorophenol	25
2-Chloronaphthalene	25
Dimethylphthalate	25
Acenaphthalene	25
2,6-Dinitrotoluene	25
Acenaphthene	25
2,4-Dinitrophenol	25
4-Methylphenol	50
2,4-Dinitrophenol	125
Diethylphthalate	25
4-Chlorophenylphenylether	25
Fluorene	25
4,6-Dinitro-2-methylphenol	125
N-Nitrosodiphenylamine	25
4-Bromophenylphenylether	25
Hexachlorobenzene	25
Pentachlorophenol	125
Phenanthrene	25
Anthracene	25
Di-n-butylphthalate	25*
Fluoranthene	25
Pyrene	25
Benzidine	25
Butylbenzylphthalate	25
3,3-Dichlorobenzidine	50
Benzo(a)anthracene	25

Table 7 (Cont.).

<u>COMPOUND</u>	<u>DETECTION LIMIT ($\mu\text{g/kg}$)</u>
Chrysene	25
Bis(2-ethylhexyl)phthalate	25
Di-n-octylphthalate	25
Benzo(b)fluoranthene	25
Benzo(k)fluoranthene	25
Benzo(a)pyrene	25
Indeno(1,2,3-cd)pyrene	25
Dibenzo(ah)anthracene	25
Benzo(ghi)perylene	25
Analine	50
Benzyl alcohol	25
Benzoic acid	25
2-Methylnaphthalene	25*
Dibenzofuran	25

* - These compounds may be listed below the detection limit due to result of blank subtraction.

consistent with past evaluations of river sediments. For the purpose of simplifying discussion in the following text sections of this report, concentrations will be reported in parts per million (ppm).

Overall Spatial Patterns

Total PNAs

As presented in Table 4, there were 16 different parent PNAs quantified (out of numerous PNAs which were alkylated isomers of these compounds) during the organics analysis of the 9 Elizabeth River sites. PNAs are commonly found in the environment as a result of chemical processing, wood treatment, combustion of fossil fuels, and various industrial processes, including coking. Many PNAs have known carcinogenic characteristics, and therefore, are of great concern where concentrations have accumulated to excessive amounts over time. Figure 22 shows the mean concentration, in $\mu\text{g/kg}$, for each site. These values represent the concentration which would be obtained if one were to take equal volume cores, to a depth of 150 cm, at all three transect sites (i.e. channel and shoals), composite the samples, and take a one kilogram dry aliquot of the composite sample for analysis. This would be similar to a mechanical dredging event where the dredge depth was 150 cm, the dredged material was well homogenized on a barge, and a one kilogram dry weight subsample taken to be analyzed for priority

pollutants. Excluding Site P, which was only sampled in the transect channel, the PNA concentrations in sediments ranged from 5,000 $\mu\text{g/kg}$ (5.00 ppm) at Site Q to 89,070 $\mu\text{g/kg}$ (89.07 ppm) at Site O. The most obvious trends seen for PNA concentrations in the River were: 1) a decrease in concentration from the Eastern Branch (Site EB) downstream to the mainstem (Site J), 2) almost regularly increasing concentrations moving upstream from Site J to Southern Branch Site O, and 3) noticeably decreasing PNA concentrations from Site O to Site Q. This trend may not be specifically dependent on the number of shoreline activities taking place, but rather on the types of land use activities occupying particular areas of the River.

Sediments from Site O stand out as being significantly more contaminated with PNAs than those collected at the other eight sites, which ranged in concentration from 5.0 ppm (station Q) to 19.52 ppm (station M). Station O, located approximately 4 miles upstream from the mouth of the Southern Branch (Site K), is flanked by an industrial site, an abandoned chemical processing industry, as well as an oil terminal slightly upstream of the site.

Total Phthalates

Although the total phthalate content at each site is lower than the total PNA content, the values are still quite high, with concentrations ranging from 0.18 ppm at station M to 3.15 ppm at station O (Fig. 23). Phthalates have a number of commercial uses,

including utilization as solvents, in vacuum pumps, in insecticide formulations, as stabilizers in most "plastic" products, etc. Phthalates are extreme irritants and may potentially have toxic, mutagenic, as well as teratogenic properties. Therefore, concentrations of this magnitude are a potential for numerous environmental effects and hazards to indigenous living resources. It is of special interest that station O, found to be highest in total PNA content, was also found to be highest in phthalate content. It is possible that the high concentrations of PNAs (potentially small particles of creosote) have the ability to concentrate other organic contaminants out of the water (i.e. miscellaneous hydrophobic organic contaminants are much more soluble in the PNA-rich sediments than in the water and would, therefore, tend to bind to these organic-laden sediment particles). There appear to be no obvious spatial trends in phthalate concentration when one looks at the entire area of evaluation covered in this study.

Organics Data by Site

Figures 24 and 25 give a view of all sites and their three transect locations. These values represent the concentration which would exist in sediments from a core for which the four depth sections had been composited. Therefore, the values represent mean concentrations, per kilogram of dry sediment, for a 0-150 cm composite core from a particular site. The values were calculated using the data presented in Table 3 and the procedure described in

the Metals section of this report (see p. 9). The data generated from these calculations indicated three general patterns. First, there appears to be a higher total PNA concentration in the right shoal (moving upstream) than in the channel or the left shoal for most sites. This may be due to the differences in numbers and types of land use between the two sides of the Southern Branch of the River (i.e. the right side is more industrialized in sections of the River). The second apparent trend is that, with the exception of sites M, O, and Q, there appears to be a lower concentration of total PNAs in the channel as compared to the two shoals. This may have been due to past dredging activities which could have eliminated many of these compounds through removal of the surface sediments. Third, there is a relatively consistent increase in total PNA content in all three transect sites as one moves upstream, with a very prominent peak in the channel and the left shoal core samples from Site O and a right shoal peak at Site M (Figs. 24 and 26).

In the following portion of the organic contaminants section each site will be evaluated for total PNAs, total phthalates, and other significant contaminants with relation to each transect site and core depth. All comments, findings, and evaluations are based on the data presented in Figures 24 and 26 for PNAs and Figures 25 and 27 for phthalates. For a complete breakdown of the total PNA and phthalate compounds, by site, transect location, and core depth refer to Volume II, Appendix D.

Figure 24. Total average concentrations of polynuclear aromatic hydrocarbons (PNAs) by site and transect location.

TOTAL PNAS IN ELIZABETH RIVER SEDIMENT BY STATION AND LOCATION

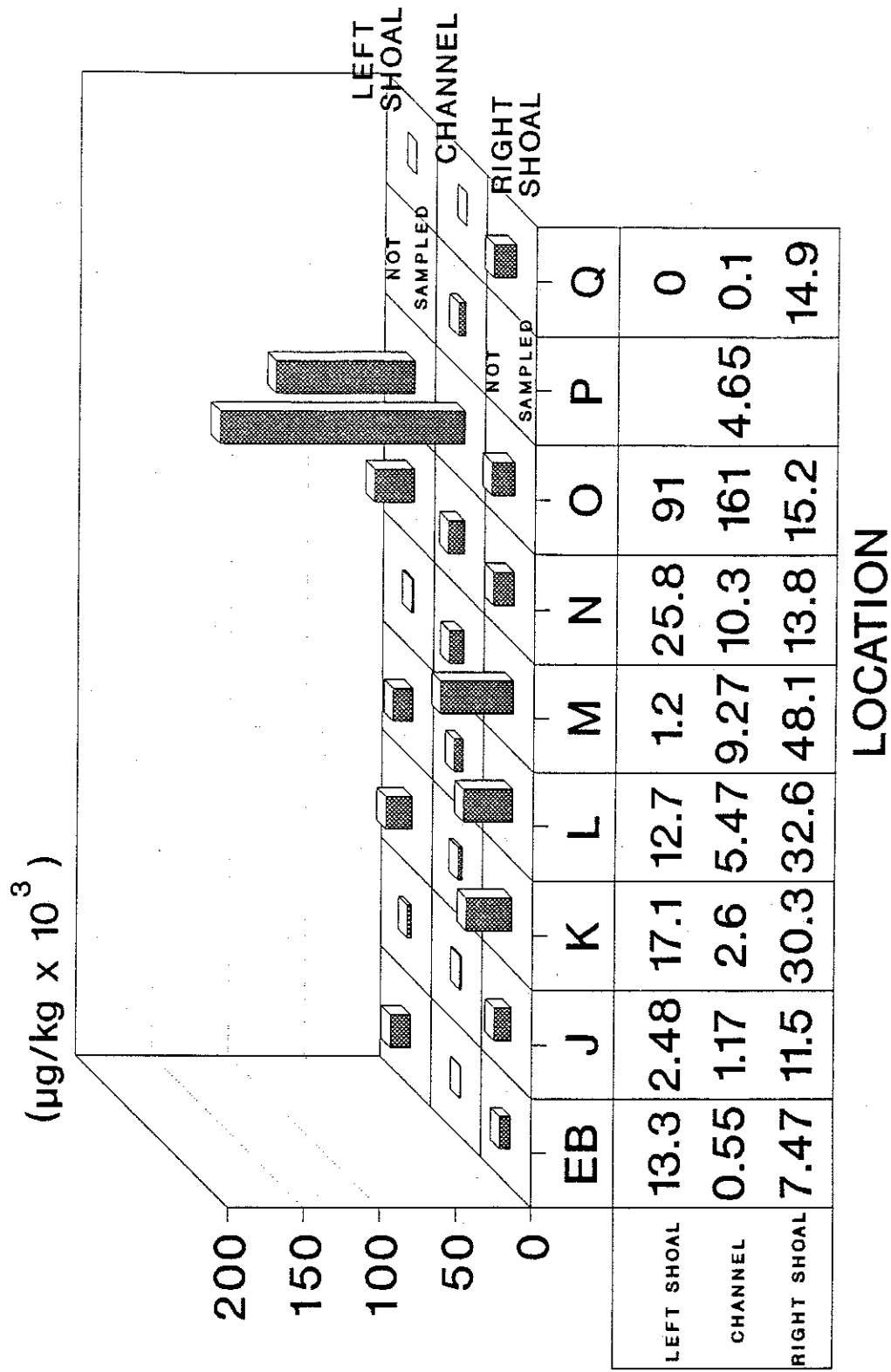


Figure 25. Total average concentrations of phthalates by site and transect location.

TOTAL PHTHALATES IN ELIZABETH RIVER SEDIMENTS

BY STATION AND LOCATION

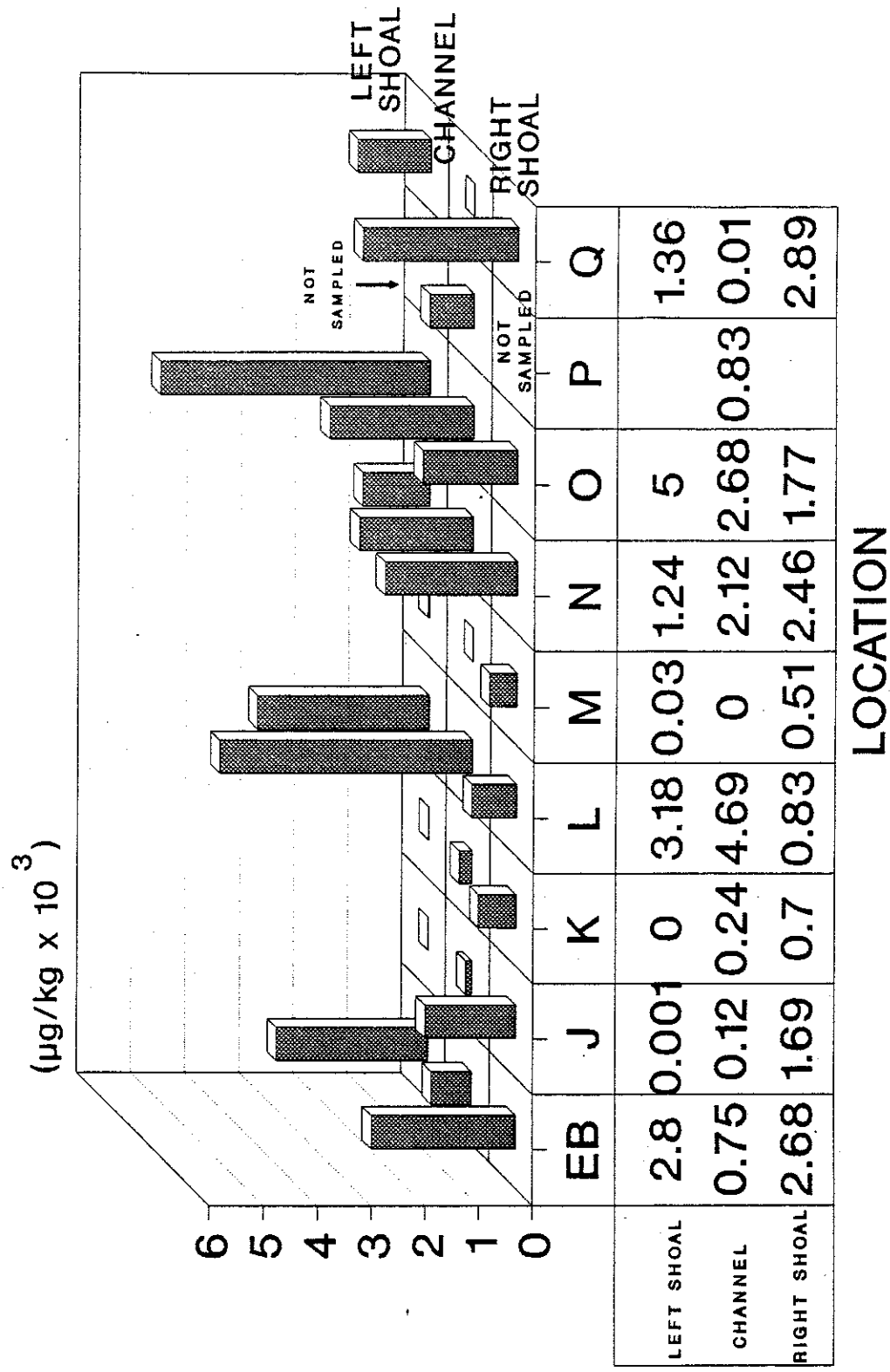
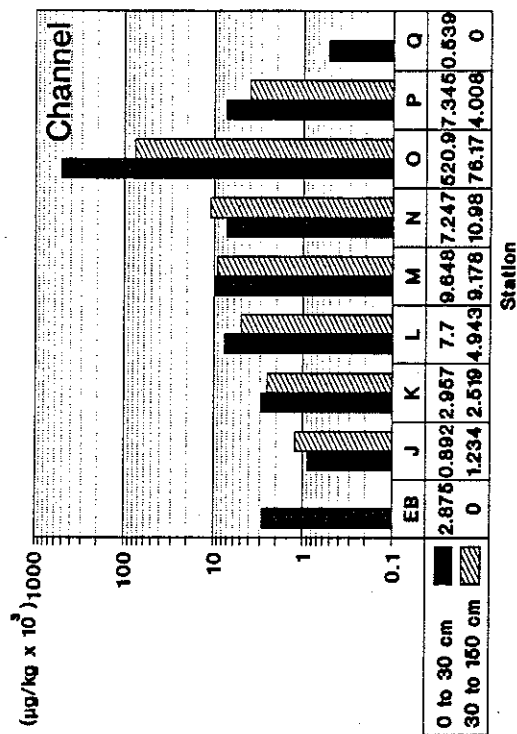
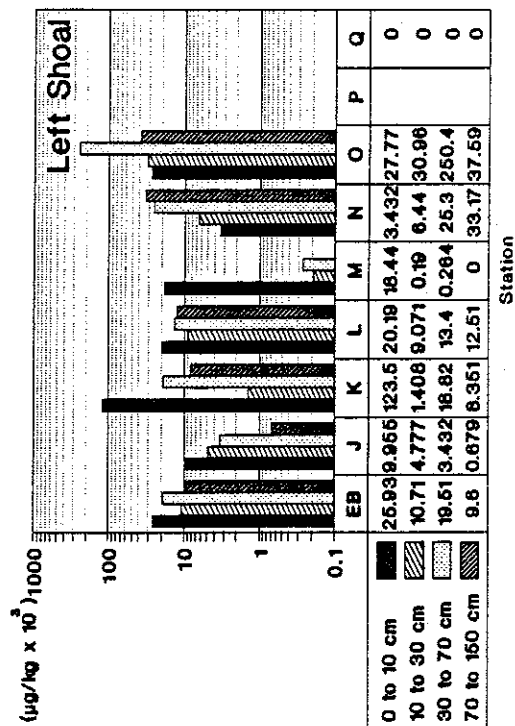


Figure 26. Total polynuclear aromatic hydrocarbons (PNAs) by site, transect location and depth. All graphs are on log scale for concentration; 0 = below detection limit.

TOTAL PNAS IN ELIZABETH RIVER SEDIMENTS BY STATION AND DEPTH



TOTAL PNAS IN ELIZABETH RIVER SEDIMENTS BY STATION AND DEPTH



TOTAL PNAS IN ELIZABETH RIVER SEDIMENTS BY STATION AND DEPTH

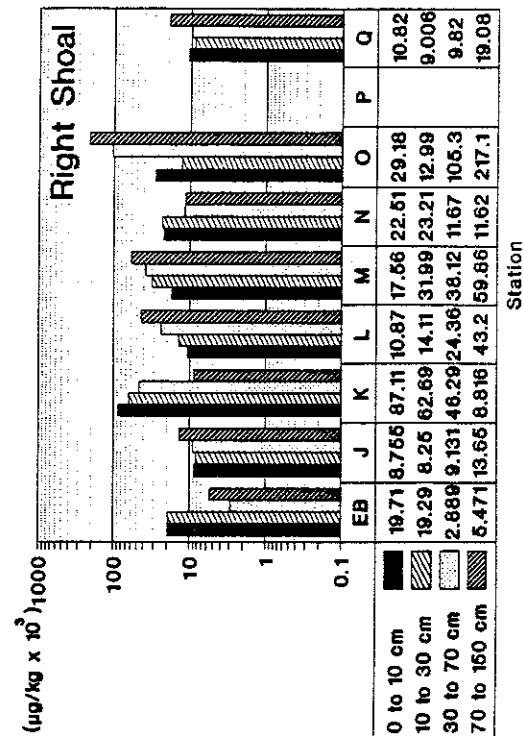
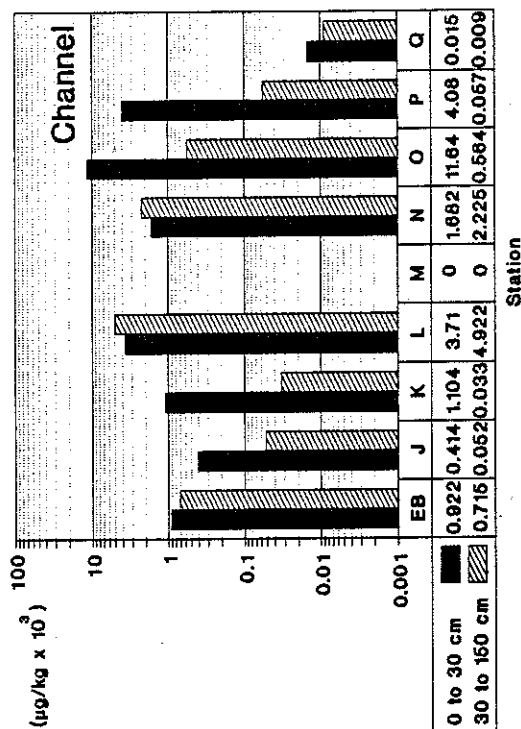


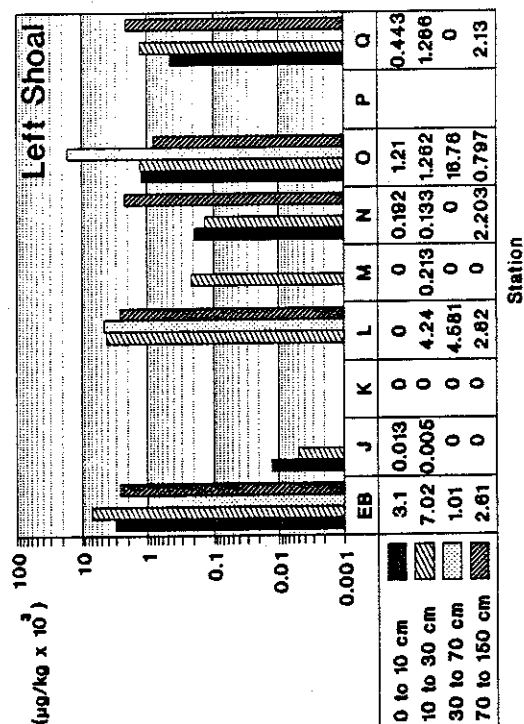
Figure 27.

Total phthalates by site, transect location and depth. All graphs are on log scale for concentration; 0 = below detection limit.

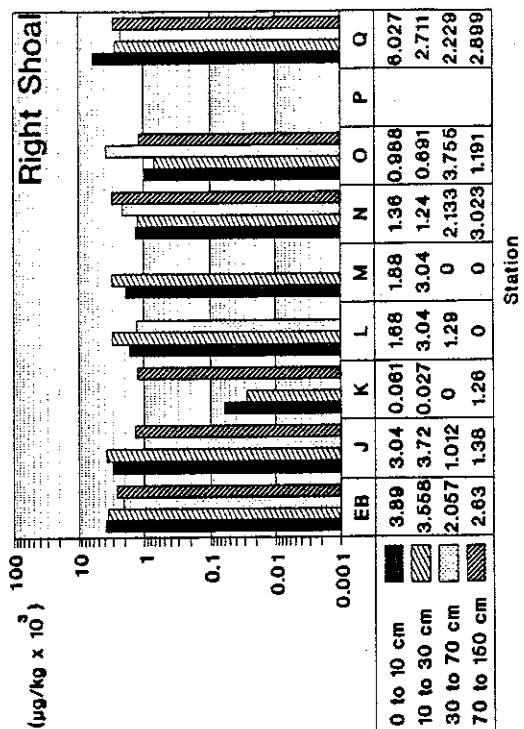
TOTAL PHTHALATES IN ELIZABETH RIVER SEDIMENTS
BY STATION AND DEPTH



TOTAL PHTHALATES IN ELIZABETH RIVER SEDIMENTS
BY STATION AND DEPTH



TOTAL PHTHALATES IN ELIZABETH RIVER SEDIMENTS
BY STATION AND DEPTH



SITE EB

PNAs

The PNA content at Site EB was found to be higher in the shoal sediments than in the channel, with the left shoal concentration being slightly higher than the right shoal. The high PNA values on both sides of this site (found approximately 1 nautical mile upstream from the mouth of the Eastern Branch of the Elizabeth River) are not surprising due to the presence of heavy shipyard activity on both sides of the water. No outstanding depth distribution patterns appeared at this site.

Phthalates

The phthalate data at Site EB correspond well with the PNA data. The two shoals are substantially higher in concentration than the channel and, as with the PNAs, the left shoal is slightly higher in concentration than the right shoal. When compared to nearby Site J, EB shoal and channel values were generally higher for phthalate content (see data for site J below). No outstanding depth patterns appear at this site.

Other Compounds

Additional compounds detected at Site EB include benzoic acid (benzenecarboxylic acid) and dibenzofuran (a known breakdown product of dioxin) in both shoals, but not in the channel. In addition, 2-methylnaphthalene (a substituted PNA) was detected in the right shoal.

SITE J

PNAs

Though the total PNA content of Site J is somewhat lower (in the channel and the left shoal) than that found at Site EB, the pattern is similar, with the shoals being higher in concentration than the channel. In addition, right shoal sediments at Site J contain almost five times the concentration of PNAs as the left shoal. This site is positioned near marina and dock facilities, as well as other commercial and residential sites. Depth distribution patterns of PNAs appear opposite for the shoals. The left shoal concentration decreased with depth in the sediment, while the right shoal concentration increased with depth to a maximum of 13.65 ppm in the 70-150 cm fraction (Fig. 26).

Phthalates

Total phthalate concentrations showed a pattern similar to that found in the PNA concentrations, where the right shoal concentration was significantly higher than the channel and left shoal concentrations. In addition, the left shoal concentration was extremely low at 0.001 ppm total phthalates per kilogram. All three transect sites showed a decrease in concentration with depth in the sediment (see Fig. 27).

Other Compounds

As observed at Site EB, dibenzofuran was detected in both of the transect shoals, but not in the channel. Furthermore, 2-methylnaphthalene was detected in all three transect sites while

two chlorophenols (pentachlorophenol and 2,4,6-trichlorophenol) were detected in the right shoal surface core only.

SITE K

PNAs

As with Sites EB and K, the transect shoals tended to be higher in PNA content than the channel sample. Further, the shoal pattern followed the pattern for Site J in that the right shoal had a significantly higher concentration than the left shoal (30.3 ppm and 17.1 ppm, respectively). The depth profile in Figure 26 indicated that the left shoal contamination was mainly in the surface sediment (0-10 cm sample). Conversely, the right shoal showed high concentrations in the top three depth fractions, but with a steady decrease with depth. There appeared to be no pattern to the particular PNA compound responsible for these shoal and depth trends. Conversely, the high surface concentration in the left shoal was mainly comprised of five PNAs (benzo(a)anthracene, benzo(b)fluoranthene, fluoranthene, phenanthrene, and pyrene) which had high 0-10 cm concentrations and very little, or no detectable amounts below this depth.

Phthalates

The spatial pattern of phthalates at this site was similar to that of Site J, with right shoal sediments having the highest concentrations, followed by the channel, and with no phthalates detected in the left shoal. The depth profile presented in Figure

27 demonstrates that the bulk of the phthalate content in the channel sediments was in the top 30 cm, while the right shoal contamination is mainly in the 70-150 cm depth.

Other Compounds

Dibenzofuran was high at Site K in comparison to most other sites. Other than the channel at Site O, the dibenzofuran content in the Site K right shoal (1.82 ppm in 0-10 cm) was the highest of all transect locations evaluated in the study. In addition, a significant amount was present in the two lowest depth fractions of the left shoal. 2-Methylnaphthalene was found in both the right and left shoals and 2,4-dimethylphenol was determined to be present in high concentration (69.8 ppm) in the top 10 cm of the left shoal.

SITE L

PNAs

All three transect sites of Site L had high concentrations of PNAs. The right shoal was highest (32.6 ppm) followed by the left shoal (12.7 ppm) and the channel (5.47 ppm). The channel composites appeared to have no outstanding compounds at either depth, although the concentration decreased with depth. The left shoal had a very high concentration of benzo(b)fluoranthene (17.60 ppm) in the top 10 cm. The most significant trend, however, at Site L was the apparent increase of PNA content with depth in the right shoal. Three compounds (acenaphthene, fluorene, and pyrene) stood out as having the greatest increase with depth, although most

of the other compounds also increased with depth. In addition, the surface sediments (0-10 cm) of the left shoal contained only two PNA compounds, while the three successively lower depths contained 10, 7, and 9 compounds, respectively. Conversely, the right shoal contained increasingly fewer PNAs with depth (14, 12, 7, and 5 compounds moving downward through the sediment column). The depth distribution patterns of PNAs at Site L may be related to the type of commercial activity on either side of the River at this site (i.e. shipyard activity and several industrial/commercial sites up- and downstream of the site) and/or the burial of a historic source of contaminants.

Phthalates

The phthalate pattern is very different from that found for PNAs at Site L. The channel site contained the highest total average phthalate concentration (4.69 ppm), followed by the left shoal (3.18 ppm) and then the right shoal (0.83 ppm). No outstanding trends appear at this site with depth.

Other Compounds

Dibenzofuran was detected in both shoals at Site L, but was not present in the channel composites. Further, the dibenzofuran detected in the left shoal was in the top 10 cm, while that detected in the right shoal was in the lowest core fraction (70-150 cm). In addition, 2-methylnaphthalene was detected in both of the shoals, and phenol was detected in the 30-70 cm fraction of the right shoal.

SITE M

PNAs

There appeared to be a very strong PNA pattern at Site M, with the right shoal being highest in concentration (48.1 ppm), followed by a significant decline in the channel (9.27 ppm) and a comparatively low concentration in the left shoal sediments (1.20 ppm). This pattern was not surprising due to the heavy shipyard activity on the right side of the River at Site M as compared to the left side. The pattern with depth was very similar to that found for Sites K and L, with left shoal sediments tending to have higher PNA concentrations at the surface and the right shoal having higher concentrations in the deeper fractions. The left shoal contained seven PNAs in the top 10 cm, one in the 10-30 cm depth, and one in the 30-70 cm depth. The right shoal had a relatively regular distribution of the PNA compounds; however, there was a substantial increase in concentration with depth for most of the compounds detected.

Phthalates

The phthalate pattern at Site M resembled the pattern for PNAs. The left shoal and the channel sediments contained low (or no) phthalate concentrations relative to the concentration in the left shoal sediments. Both shoals contained the phthalates in the top 30 cm of the core sample.

Other Compounds

As with Site L, dibenzofuran was detected in the top 10 cm of

the left shoal and in the 70-150 cm section of the right shoal core at concentrations similar to those seen in Site L. In addition, 2-methylnaphthalene was also detected in the surface section of the left shoal and the 70-150 cm section of the right shoal core.

SITE N

PNAs

The PNA content of the Site N transect sites appeared to be almost opposite of the pattern found at Site M, the adjacent downstream site. The highest concentration was found in the left shoal, with the channel and the right shoal sediments having significantly lower concentrations. However, the total average concentrations at all three transect locations were high, ranging from 10.3 ppm to 25.8 ppm. This pattern may be due to the presence of chemical processing industries on both sides of the River in the vicinity of the site. The left shoal showed a different pattern than that found in the left shoals of Sites L and M, i.e. the concentrations of total PNAs tended to increase, rather than decrease, with depth in the sediments on the left shoal of Site N (3.432 ppm in the top 10 cm to 33.17 ppm in the 70-150 cm depth (see Fig. 44). PNA concentrations in right shoal sediments tended to be high in the top 30 cm and approximately 50% lower in the 30-150 cm depths.

Phthalates

The phthalate concentration of the right shoal of Site N was

found to be the highest, followed by the channel and then the left shoal. However, all concentrations were very similar at the transect sites, ranging from 1.24 ppm to 2.46 ppm. All three transect locations had higher concentrations of total phthalates in the lower core depths.

Other Compounds

Dibenzofuran was detected in the surface 10 cm and in the 70-150 cm samples of the left shoal and, as with Sites L and M, in the 70-150 cm core section of the right shoal. In addition, 1,3-dichlorobenzene, 2-methylnaphthalene, and n-nitrosodiphenylamine were detected in the right shoal of Site N.

SITE O

PNAs

Site O stands out in PNA concentration patterns in two respects. First, unlike any of the other sites evaluated during this project, the channel concentrations were significantly higher than both of the shoal sites. Second, the concentrations of total PNAs in both the channel and the left shoal sites were significantly higher than those determined in the other eight sites, and actually exceed the sum concentration of PNAs for the corresponding transect location at the other 8 sites. This may be due to the presence of a nearby industrial site, an abandoned chemical processing industry, and an oil terminal slightly upstream of the site. Five PNA compounds had extremely high concentrations

at this site. Benzo(a)anthracene was determined to be present at a concentration of 89.90 ppm in the 30-70 cm core section of the left shoal and 118.0 ppm in the top 30 cm of the channel. Benzo(a)pyrene was found to be 68.00 ppm in the 30-70 cm core section of the left shoal and 83.30 ppm in the top 30 cm of the channel. Benzo(k)fluoranthene was detected at a concentration of 185.0 ppm in the top 30 cm of the channel and 81.90 ppm in the 70-150 cm depth of the right shoal. Chrysene was found in the top 30 cm of the channel at a concentration of 108.0 ppm. Pyrene was detected at high concentrations in the 30-70 cm core section of both the left shoal (58.80 ppm) and the right shoal (35.40 ppm). In addition to these compounds, most of the other PNAs listed in Table 4 were detected in most of the depth fractions of all three transect sites, but at lower concentrations (see Appendix D). On the left shoal the greatest total PNA concentration was found in the 30-70 cm depth (250.4 ppm), with the other core fractions combined totaling less than half of the concentration found at this depth. The majority of the PNA concentration in the channel was found in the top 30 cm (520.9 ppm) while the right shoal contains most of its PNA content in the 30-70 cm and 70-150 cm depths (105.3 and 217.1, respectively).

Phthalates

Phthalate concentrations did not show the same overall pattern as the PNA concentrations at Site O. The highest concentration was found in the left shoal followed by the channel and then the right

shoal. However, the depth trends are similar to those found for PNAs. The highest concentrations were found in the left shoal 30-70 cm depth, in the surface 30 cm of the channel, and in the 30-70 cm and 70-150 cm depths of the right shoal. The high concentration in the 30-70 cm depth of the left shoal is mainly attributed to 16.70 ppm of bis(2-ethylhexyl)phthalate.

Other Compounds

Dibenzofuran was found, in varying concentrations, in all depths of all three transect locations. The highest total dibenzofuran concentration for all nine sites was found in the channel of Site O. 1,3-Dichlorobenzene, 1,4-dichlorobenzene, and 2-methylnaphthalene were also detected at Site O.

SITE P

PNAs

The discussion of trends at Site P is limited to patterns in the channel due to the lack of data from the shoal sites. The total average PNA concentration of 4.65 ppm was attributable to a concentration of 7.345 ppm in the top 30 cm and 4.008 ppm in the 30-150 cm depth.

Phthalates

The total average phthalate concentration (0.83 ppm) was found mainly in the 4.080 ppm of di-n-butylphthalate detected in the top 30 cm of the core.

Other Compounds

Dibenzofuran was detected in both channel composite samples, 1,2-dichlorobenzene was detected in the top 30 cm, and 1,3-dichlorobenzene was detected in the 30-150 cm core section.

SITE Q

PNAs

Almost all of the PNAs found at Site Q were detected in the right shoal, adjacent to a power plant. No PNAs were detected in the left shoal and very little was detected in the channel sediments. However, a total average concentration of 14.90 ppm was detected in the right shoal. This right shoal concentration was relatively evenly distributed throughout the four core depths with the highest concentration in the 70-150 cm depth. It should be noted that this site may have been dredged just prior to sample collection.

Phthalates

Total phthalates were found to be high in both the right and left shoal transect sites. Very little phthalate contamination (0.01 ppm) was observed in the channel. The highest concentration found in the right shoal was in the top 10 cm fraction and in the 70-150 cm sample from the right shoal (6.027 ppm).

Other Compounds

Benzoic acid, dibenzofuran, and 2-methylnaphthalene were detected at various depths of the right shoal only. No additional

organic priority pollutants, other than those mentioned above, were found in the channel or the left shoal of this site.

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TOTAL ORGANIC CARBON

Results of the Total Organic Carbon (TOC) analyses are presented in Figures 28 and 29. The data plotted in Figure 28 represent the total average concentrations of TOC calculated for the total 150 cm-deep core collected from each of the nine sites (see **Metal Contaminants** section, p. 9, for details on the procedure for calculating these values). TOC content of the sediments was only moderate (i.e. usually <5%) throughout the Elizabeth River except at the left shoal of Site EB, where the average TOC content was 15% (8-9% in the upper 30 cm to approximately 17% in the deeper fractions; see Fig. 29). The greater TOC content of these sediments may reflect the close proximity of this sampling location to marshes along the northern shore of the Eastern Branch. No other noteworthy spatial patterns in TOC data were observed.

Figure 28.

Total organic carbon content (% TOC) in Elizabeth River sediments by site and transect location. Values represented by each bar are the percent content averaged across all depth fractions of the core sample to a depth of 150 cm.

TOTAL ORGANIC CARBON, ELIZABETH RIVER **BY STATION AND LOCATION**

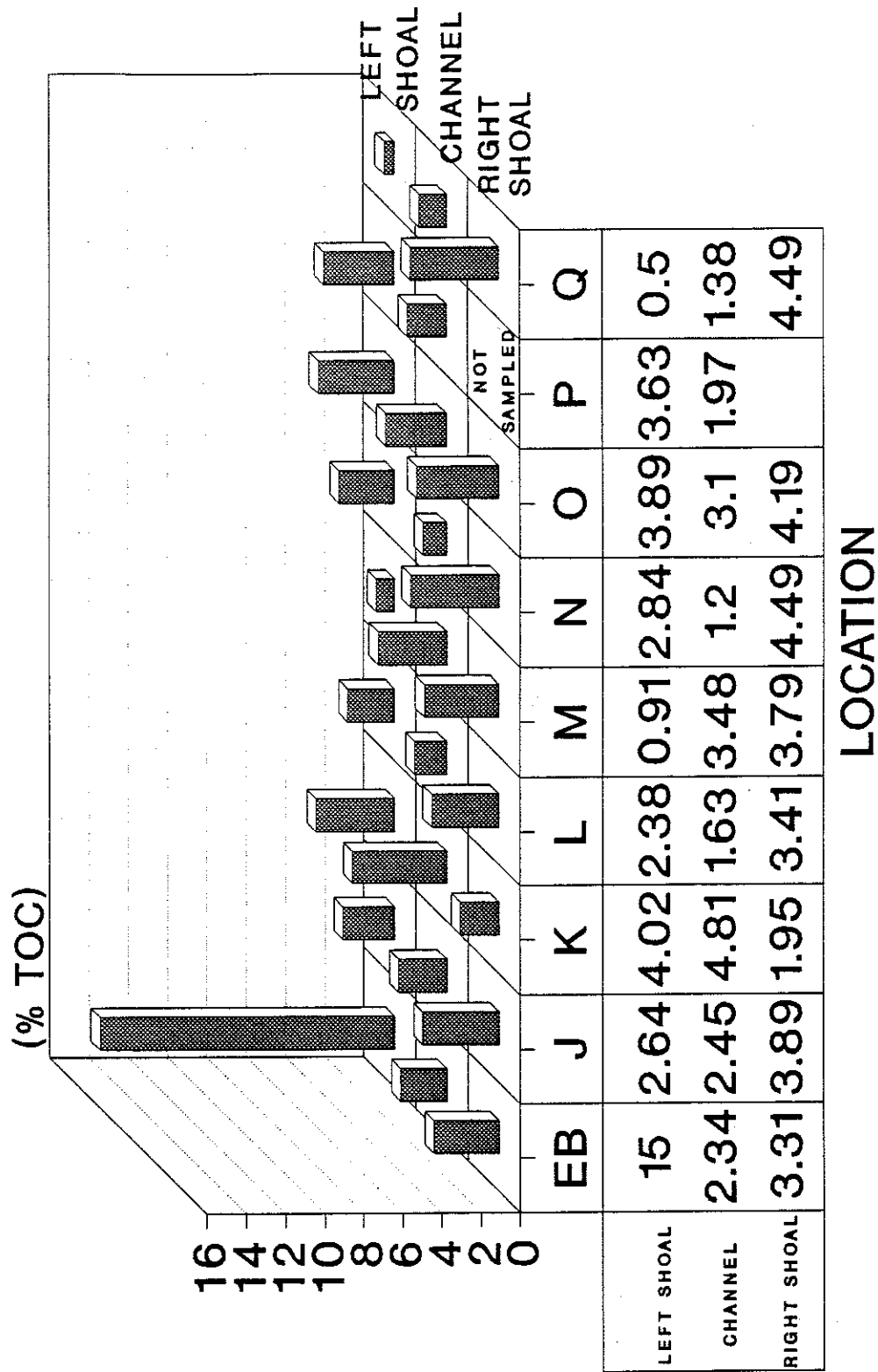
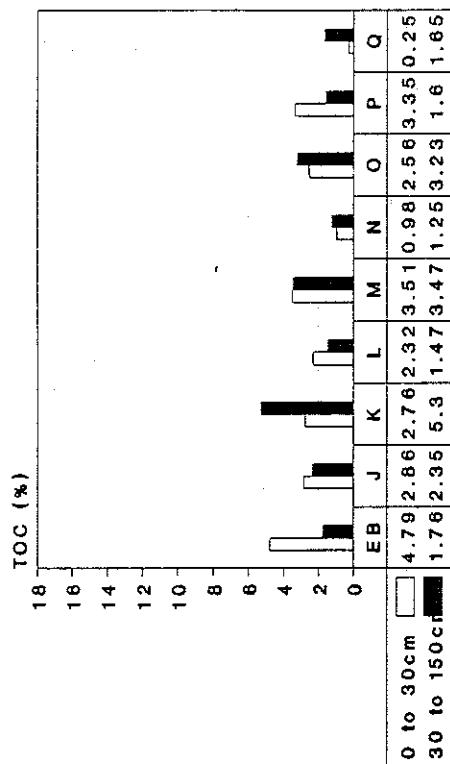


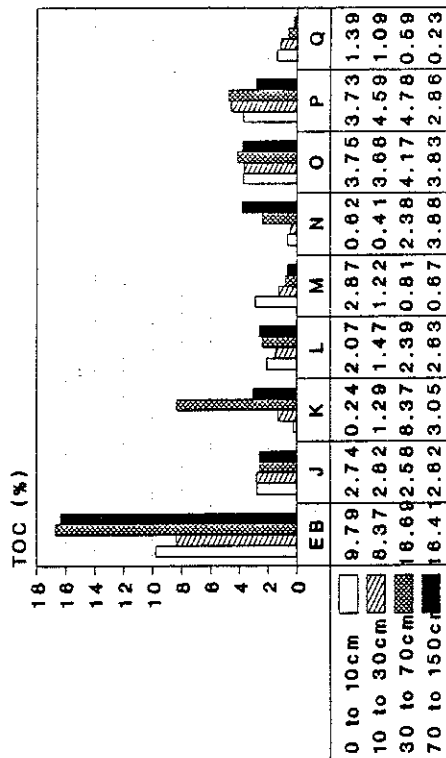
Figure 29. Total organic carbon content (% TOC) in Elizabeth River sediments by core sample depth interval, site and transect location.

Total Organic Carbon in Sediments Elizabeth River (Channel)



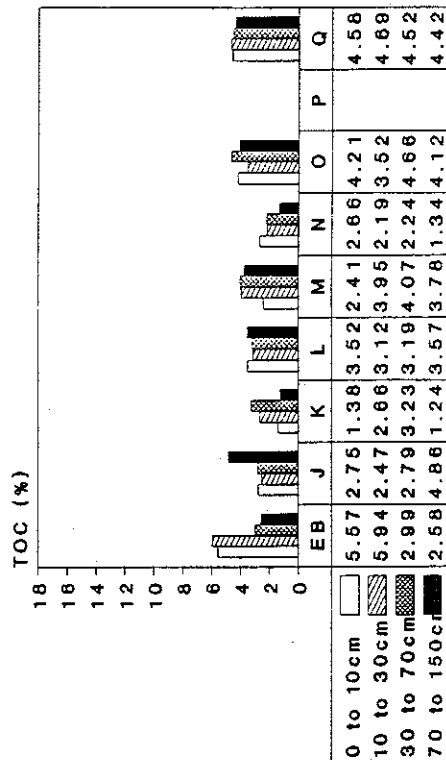
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Total Organic Carbon in Sediments Elizabeth River (L. Shoal)



Stations

Total Organic Carbon in Sediments Elizabeth River (R. Shoal)



Stations

LONG-TERM TEMPORAL PATTERNS

During the period from 1979 to 1983, a series of sediment quality studies were conducted for the U.S. Army Corps of Engineers (USACOE) at the same sites as those examined in the present study. There were certain differences in the sampling and analytical procedures of the two studies: 1) sediment collections for the USACOE studies were made with a Ponar grab, while those for the present study were taken to a depth of 1.5 m with a Vibracore; 2) the organic contaminants examined during the USACOE studies were confined to 16 PNAs (analyzed by GC, with approximately 25% confirmation by GC/MS), while all organic "priority pollutants" were analyzed in the present study with GC/MS. Nonetheless, the two data sets allowed a "big picture" comparison in the sediment contamination patterns which may have occurred on the 8 - 10 year intervening period. In order to make the data sets comparable, only the surface layer (0 - 10 cm) concentrations from the present study were used, since this interval represents the approximate effective depth of sampling for the Ponar grab (Ewing et al., 1988). The data from the USACOE studies have been previously reported for the metals (collected in 1979 and reported in Alden et al., 1981; Rule, 1986) and for the organics (collected in 1982 and reported in Alden and Hall, 1984). It should be noted that the comparisons in the following sections are preliminary in nature and the interpretation of the patterns may change if factors such as sediment grain size and organic carbon content have varied

significantly between the data sets. The presence and influence of changes in such factors are now being explored.

Metals

In addition to the statistical comparisons of 1979 data to those of the present study (described above), references are made in the following discussion to an EPA investigation of metals in sediments conducted throughout the Elizabeth River in 1974 (Johnson and Villa, 1976). The 1974 data were not obtained for use in the statistical evaluation of long-term temporal patterns, thus the concentrations of various metals reported by Johnson and Villa (1976) are presented here for the sole purpose of expanding the historical review period. That is, qualitative comparisons of these 1974 metals data to the 1979 and 1989 data are not suggested to be representative of any statistically significant changes (increases or decreases) in concentrations over the 15 year period.

Cadmium

The cadmium concentrations in the surface sediments of the Elizabeth River appeared to have decreased from 1974 to 1989 (Table 8; Figs. 30, 31). The grand mean of cadmium in the 1979 samples was 1.69 mg/kg, while that of the 1989 samples was 0.93 mg/kg, and the difference was highly significant ($p < 0.001$) when compared with a paired t-test. The greatest decrease appeared to occur in the shoal areas of Sites J-M. Of course, it should be noted that the channel samples for 1989 were taken to a depth of 30 cm, so any

Table 8. Average metal concentrations in surface sediments of the Elizabeth River. All values are mg/kg.

<u>Metal</u>	<u>1974¹</u>	<u>1979²</u>	<u>1989³</u>
Cadmium	3.5	1.69	0.93
Chromium	44	45	42
Copper	65.2	103	145
Iron	28,417	31,056	24,230
Lead	91.2	145.9	123.3
Mercury	0.22	-	0.67
Nickel	-	34.7	25.1
Zinc	379	379	387

Notes:

¹values reported in Johnson & Villa, 1976.

²Alden et al., 1981; Rule, 1986.

³Current study.

Figure 30. Change in cadmium concentrations in Elizabeth River sediments from 1979 to 1989.

CHANGE IN CADMIUM CONCENTRATIONS IN SEDIMENTS FROM 1979 TO 1989

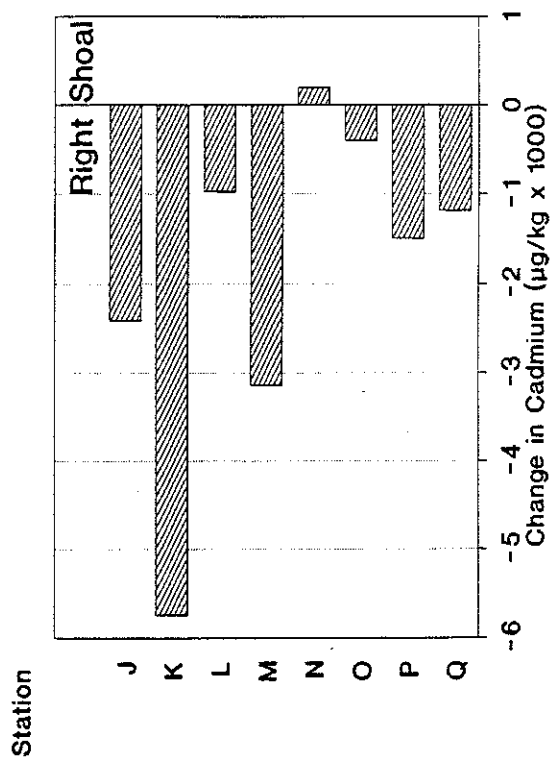
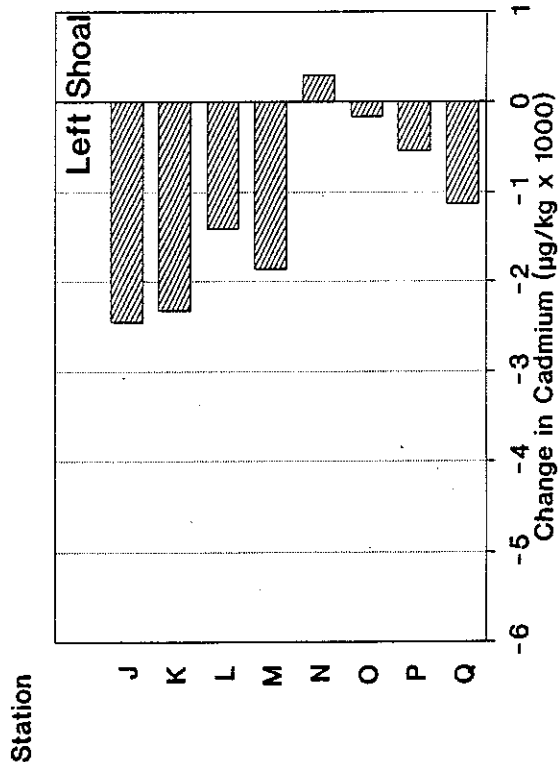
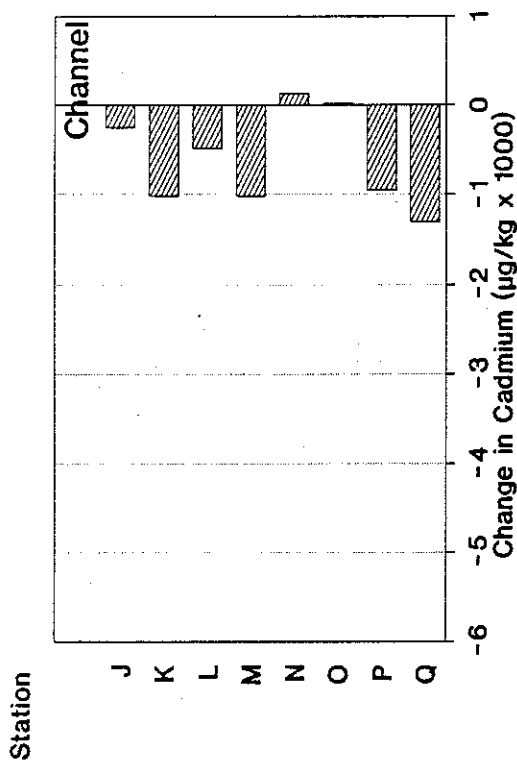
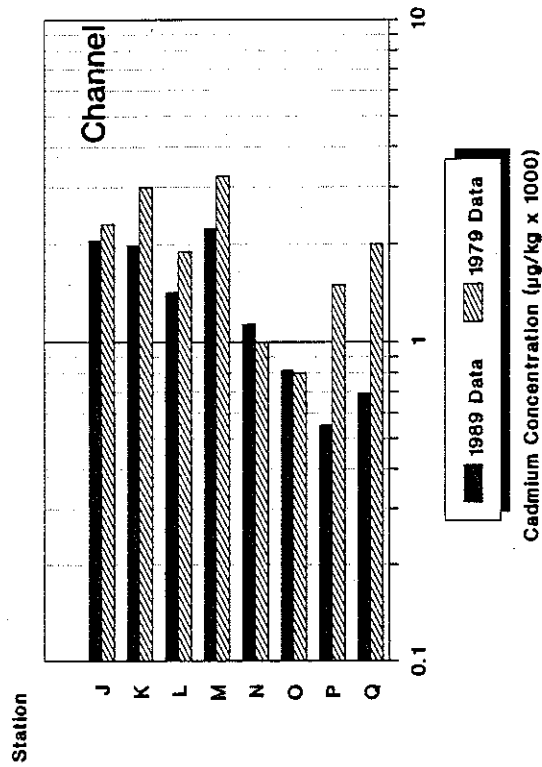
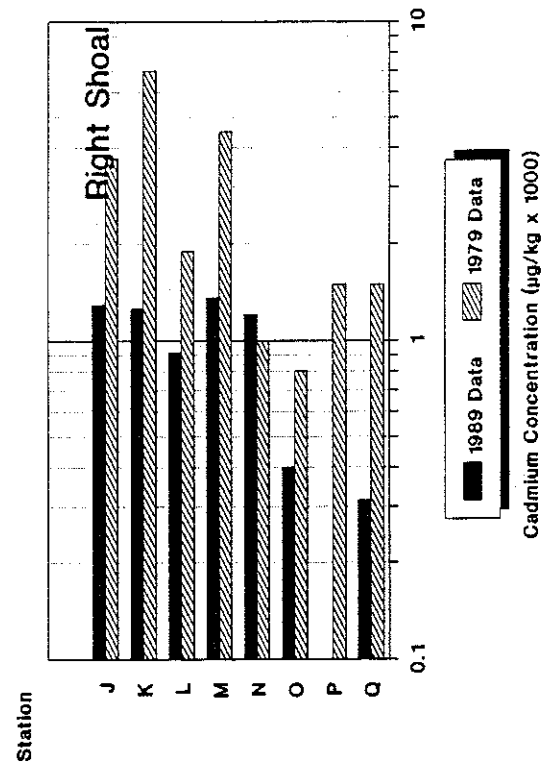
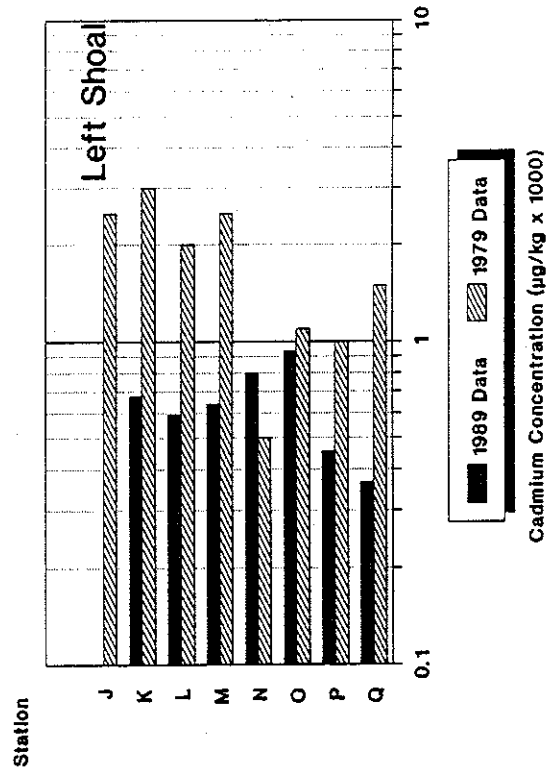


Figure 31. Comparison of cadmium concentrations in Elizabeth River sediments between 1979 and 1989.

CADMIUM IN ELIZABETH RIVER SEDIMENTS



CADMIUM IN ELIZABETH RIVER SEDIMENTS CADMIUM IN ELIZABETH RIVER SEDIMENTS



changes that might have occurred since 1979 could have been moderated by the fact that deeper sediments were included in the later collections. Likewise, dredging activities may influence this sort of comparison over time. The apparent decrease in cadmium in the sediments could be due to decreased utilization of cadmium in industrial processes and/or the effective implementation of control technologies (e.g. TMP's for NPDES permits, BMP actions, etc.) The cadmium patterns observed with depth (Fig. 12) also tended to substantiate these speculations since surface concentrations were considerably lower than those of greater depths, suggesting decreased input and burial of more "historic" contamination by sedimentation. Likewise, cadmium concentrations observed in the present study were less than those reported by Johnson and Villa (1976) for subsurface sediments in 1974.

Chromium

Chromium concentrations in surface sediments decreased very slightly from 1974 to 1989 (Table 8). The decrease from a 1979 grand mean of 45 mg/kg to a 1989 grand mean of 42 mg/kg (Figs. 32, 33) was statistically significant ($p=0.04$) and appeared to be most greatly manifested at Sites K, M, and Q. The former two sites are located in regions of shipyard activities, while the latter site is in the vicinity of a power generating plant. As with cadmium, the apparent decrease in chromium in the sediments may be due to more effective control of the release of this metal from industry. The depth distribution of chromium (Fig. 13), particularly in the shoal regions of these sites, tends to substantiate this trend, since

surface concentrations are generally lower than those observed at greater depths (i.e. recent input rates would appear to be less than previous ones). However, the chromium concentrations in surface sediments did appear to increase at Sites N and O, although the levels generally were not as great as the 1979 concentrations at K, M, and Q.

Copper

Copper concentrations in surface sediments were shown not to have changed significantly ($p=0.80$) when all samples were considered. The 1979 grand mean for copper in sediments was 103 mg/kg, while 1989 mean was 145 mg/kg (Figs. 34 and 35). However, the mean concentration of copper in 1989 was more than two times higher than reported by Johnson and Villa (1976) for samples collected in 1974 (Table 8). The largest apparent increase was observed for the right shoal samples from Sites L and P. Any interpretation of the elevated copper in the Site M channel sample must be tempered by several factors: the greater depth of the 1989 samples may have incorporated the influences of events prior to 1979 (although the greatest depth of 30-70 cm did not reflect the same level of copper, so the source events must have been relatively recent); the effects of dredging and/or ship traffic on the distribution of contaminants in the channel are unknown and likely to be complex; and single samples with highly elevated concentrations may reflect small scale spatial heterogeneity of contaminants (e.g. paint chips, or other concentrated sources of metals in a particular sample). Nonetheless, Site M is in the

Figure 32. Change in chromium concentrations in Elizabeth River sediments from 1979 to 1989.

CHANGE IN CHROMIUM CONCENTRATIONS IN SEDIMENTS FROM 1979 TO 1989

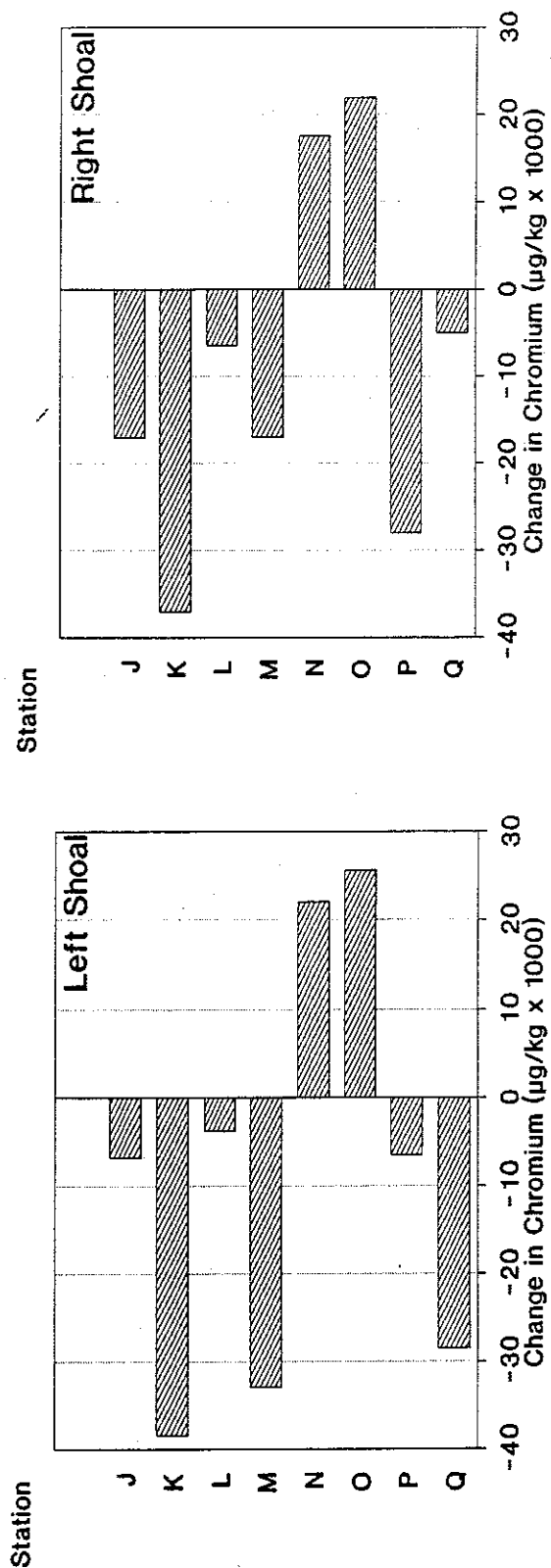
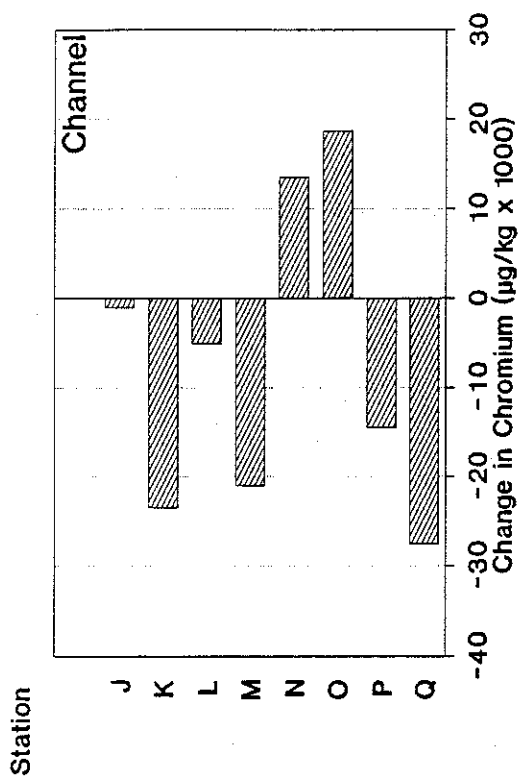
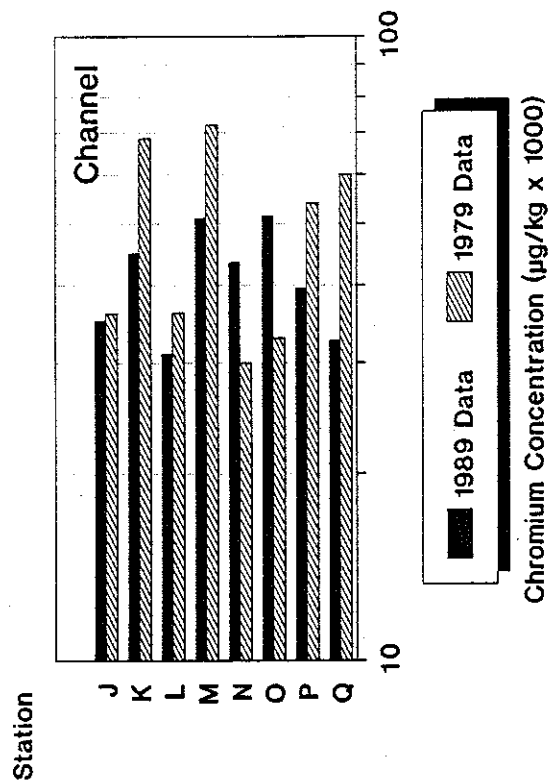
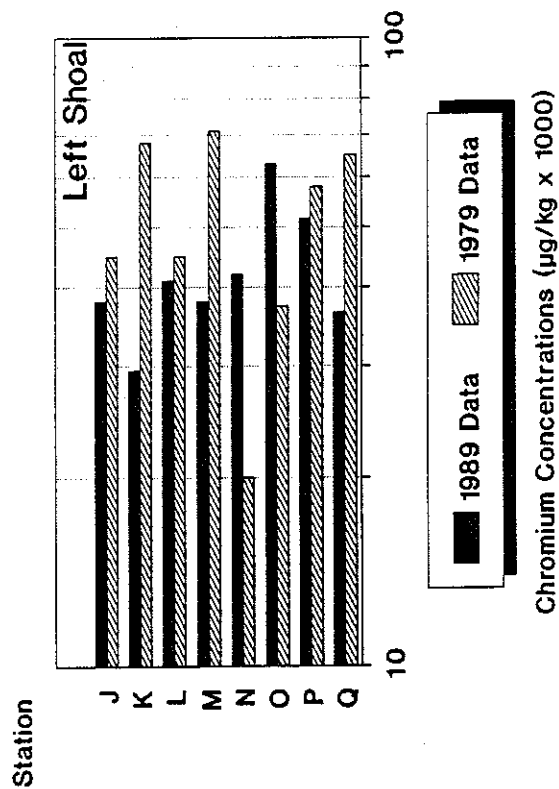


Figure 33. Comparison of chromium concentrations in Elizabeth River sediments between 1979 and 1989.

CHROMIUM IN ELIZABETH RIVER SEDIMENTS



CHROMIUM IN ELIZABETH RIVER SEDIMENTS



CHROMIUM IN ELIZABETH RIVER SEDIMENTS

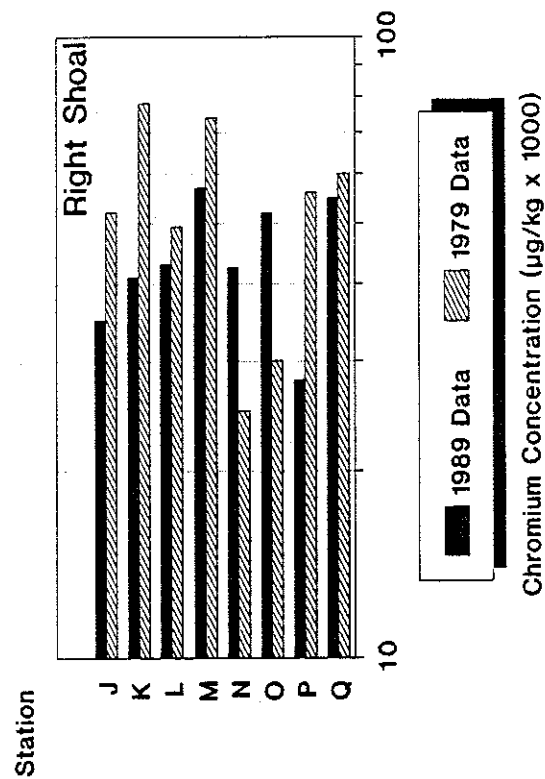


Figure 34. Change in copper concentrations in Elizabeth River sediments from 1979 to 1989.

CHANGE IN COPPER CONCENTRATIONS IN SEDIMENTS FROM 1979 TO 1989

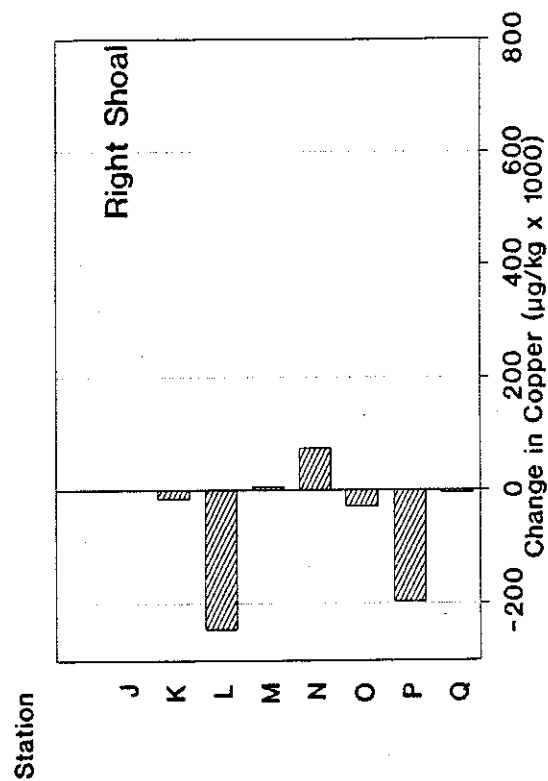
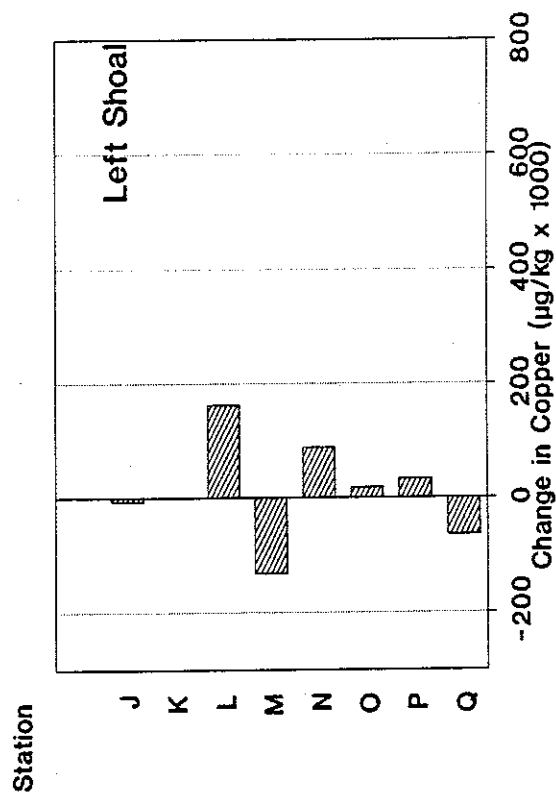
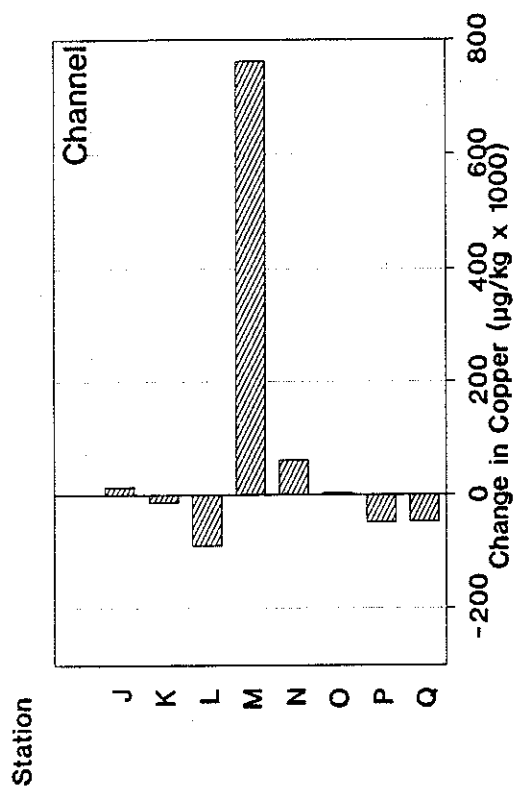
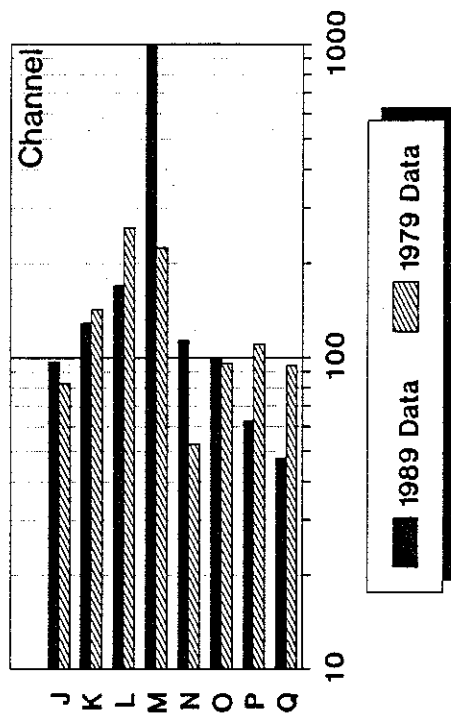


Figure 35. Comparison of copper concentrations in Elizabeth River sediments between 1979 and 1989.

COPPER IN ELIZABETH RIVER SEDIMENTS

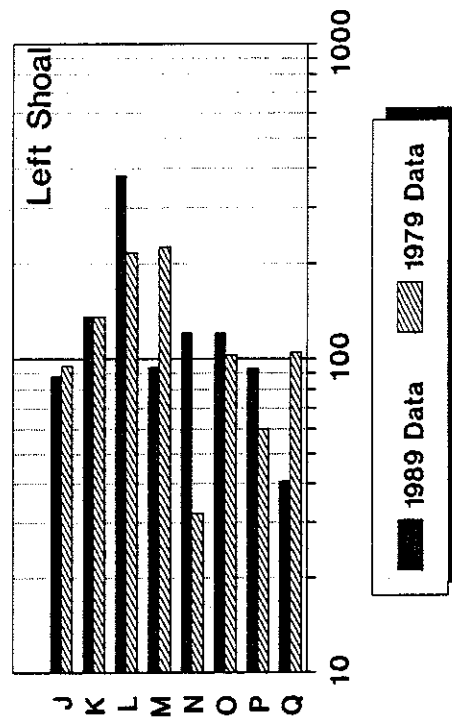
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Copper Concentration (µg/kg x 1000)

COPPER IN ELIZABETH RIVER SEDIMENTS

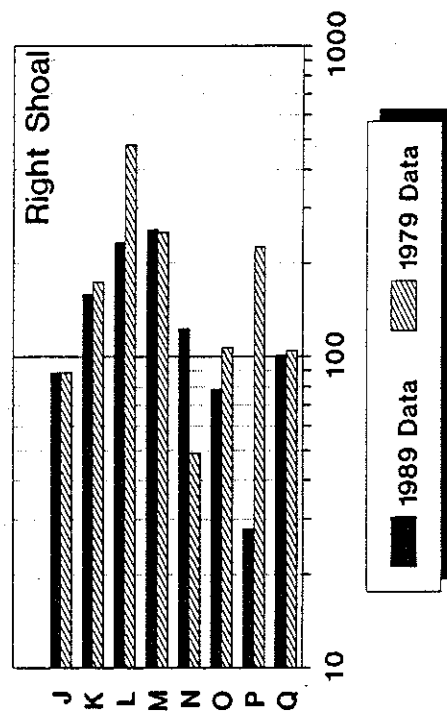
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Copper Concentration (µg/kg x 1000)

COPPER IN ELIZABETH RIVER SEDIMENTS

Station



Copper Concentration (µg/kg x 1000)

vicinity of intense shipyard and shipping activities and copper-based paints have been the most commonly used substitute for the older lead-based and organotin-based antifouling paints, so the elevated concentrations may reflect these potential sources. The 1974 grand mean for copper in near surface sediments (5-15 cm) of the Southern Branch was approximately 75 mg/kg (Johnson and Villa, 1976), possibly supporting this speculation concerning recent changes in use patterns. Of particular note was the increase in copper concentrations at Site EB. Although no 1979 data were available for this area, the 1989 copper concentrations in this region were up to two times those reported by Johnson and Villa (1976). It is interesting to note that this site was the only one displaying a significant influx of copper into the sediment in the study on metal fluxes (following section of this report).

Iron

The mean concentration of iron in sediments of the Elizabeth River in 1974 was 28,417 mg/kg (Johnson and Villa, 1976) (Table 8). Concentrations of this metal significantly decreased ($p < 0.001$) from a grand mean of 31,056 mg/kg in 1979 to a grand mean of 24,230 mg/kg in 1989 (Figs. 36, 37). Except for increases observed for Site N samples, iron decreased in all regions. Assuming that the change is not associated with a basin-wide change in the sediment characteristics (and associated geochemistry), the decreases in iron concentrations may also be due to increased control actions (e.g. NPDES permitting, BMPs of point and nonpoint sources, etc.).

Lead

The mean concentration of lead in sediments of the Elizabeth River was 91.2 mg/kg in 1974 (Johnson and Villa, 1976) (Table 8). Lead concentrations in surface sediments decreased somewhat ($p=0.03$) from a grand mean of 145.9 mg/kg in 1979 to a grand mean of 123.3 mg/kg in 1989 (see Figs. 38, 39). Decreases were observed throughout transects taken at Sites K, L, P, and Q. The right shoal samples from Sites M, N, and O displayed increased concentrations of lead compared to 1979. However, the absolute concentrations of lead at Site M (located in the vicinity of a shipyard) were much higher than those observed for N or O. There could be several possible reasons for the apparent decrease in lead in surface sediments. The widespread use of lead-free gasoline would tend to decrease the atmospheric and urban runoff sources of lead to the River. The ban on lead-based antifouling paints would also tend to decrease input from shipping and shipyard activities (although older and foreign ships may still represent a significant source of lead). The increased effectiveness of control strategies discussed previously could also explain a decrease in lead accumulation in surface sediments. Historic sources of lead input such as the abandoned foundry site located in Portsmouth (believed to be responsible for much of the high concentrations of lead in the vicinity of Site L) also should become of decreasing importance as contaminated sediments are buried by natural sedimentation processes. The depth distributions of lead (Fig. 16) in the shoal areas of Sites K-M suggest this trend may be taking place, since

Figure 36. Change in iron concentrations in Elizabeth River sediments from 1979 to 1989.

CHANGE IN IRON CONCENTRATIONS IN SEDIMENTS FROM 1979 TO 1989

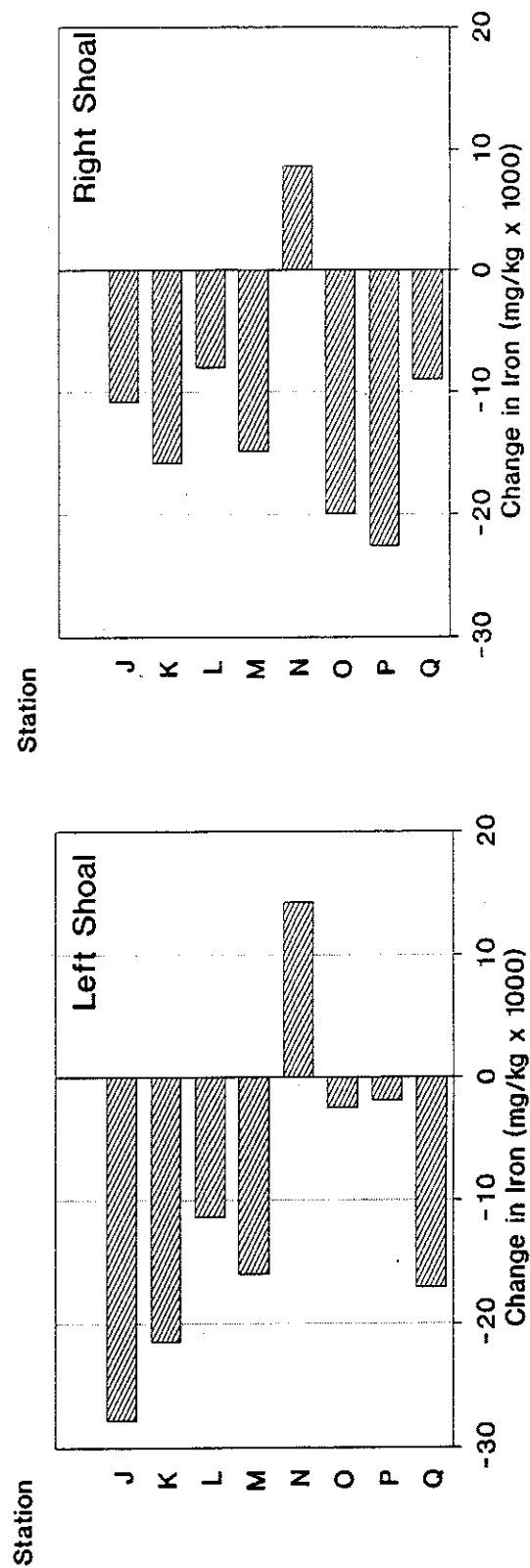
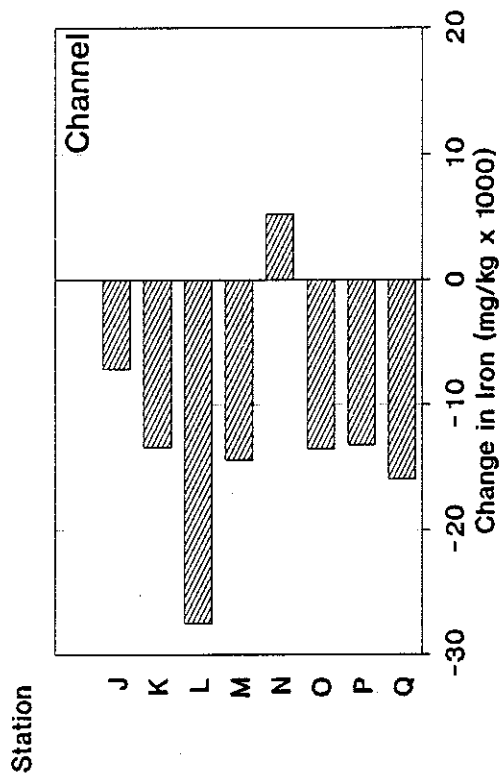
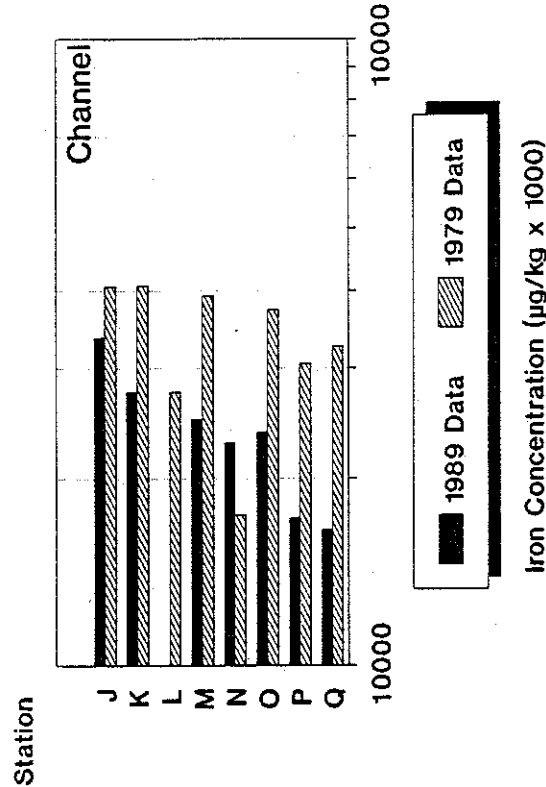
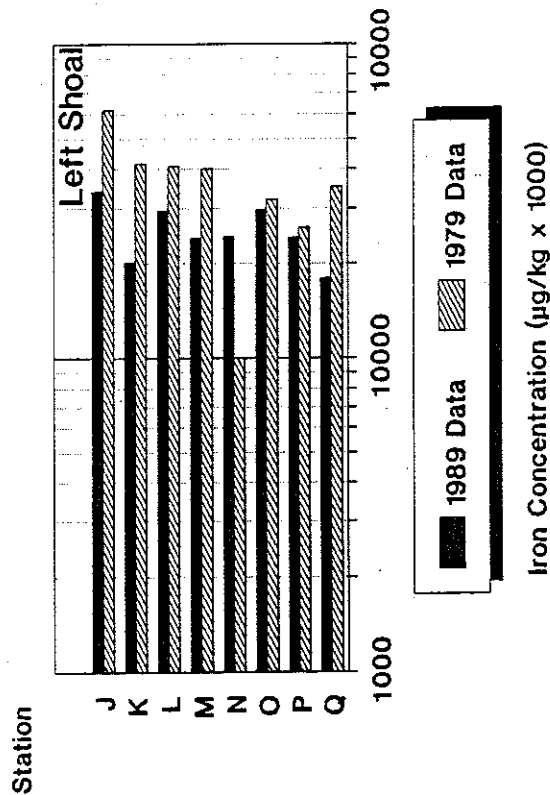


Figure 37. Comparison of iron concentrations in Elizabeth River sediments between 1979 and 1989.

IRON IN ELIZABETH RIVER SEDIMENTS



IRON IN ELIZABETH RIVER SEDIMENTS



IRON IN ELIZABETH RIVER SEDIMENTS

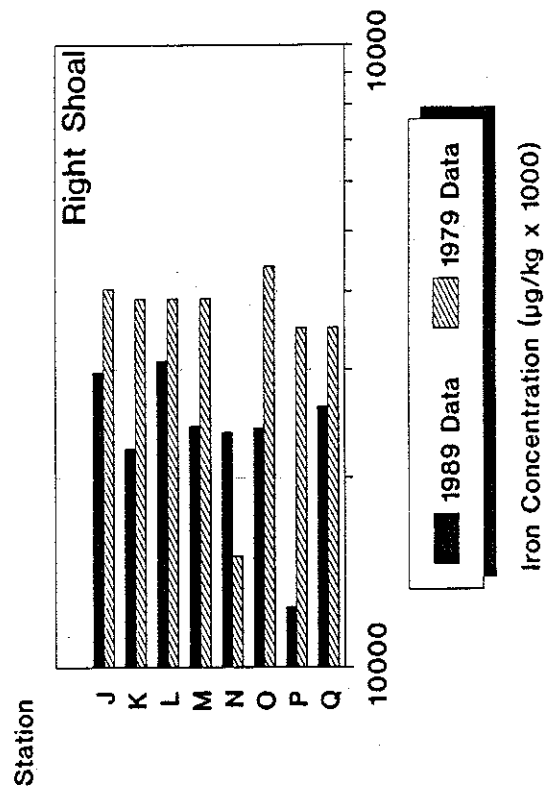


Figure 38. Change in lead concentrations in Elizabeth River
sediments from 1979 to 1989.

CHANGE IN LEAD CONCENTRATIONS IN SEDIMENTS FROM 1979 TO 1989

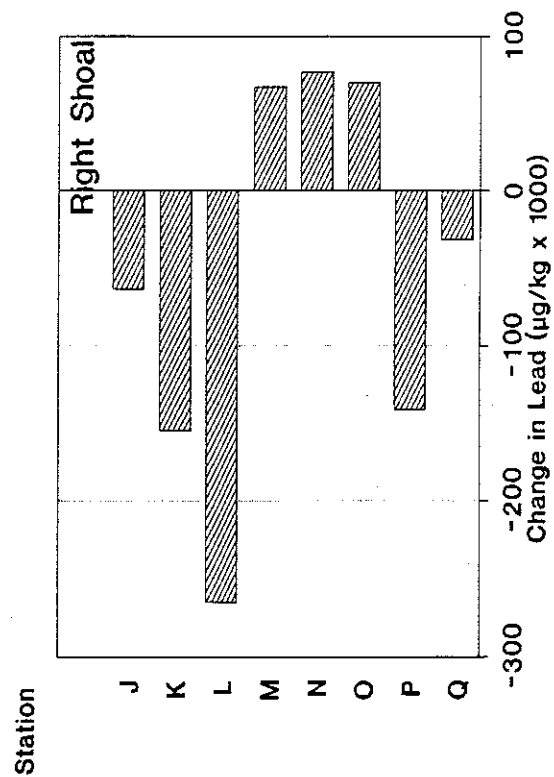
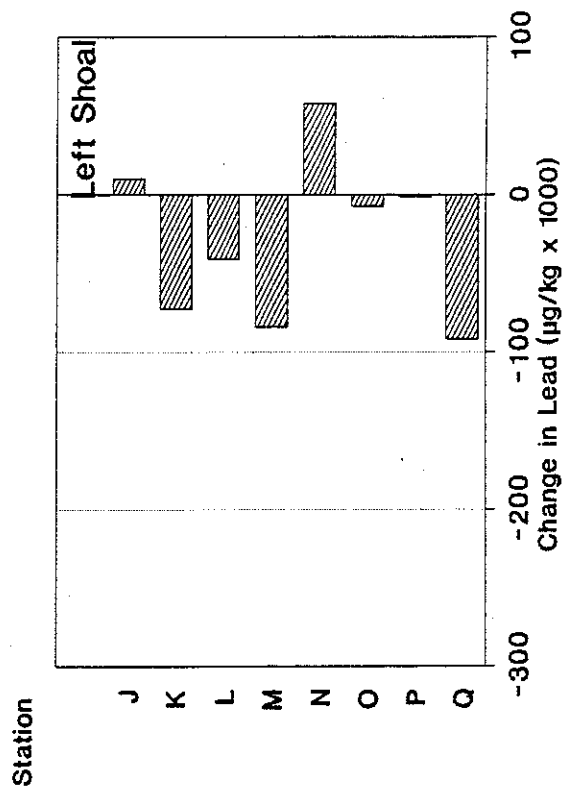
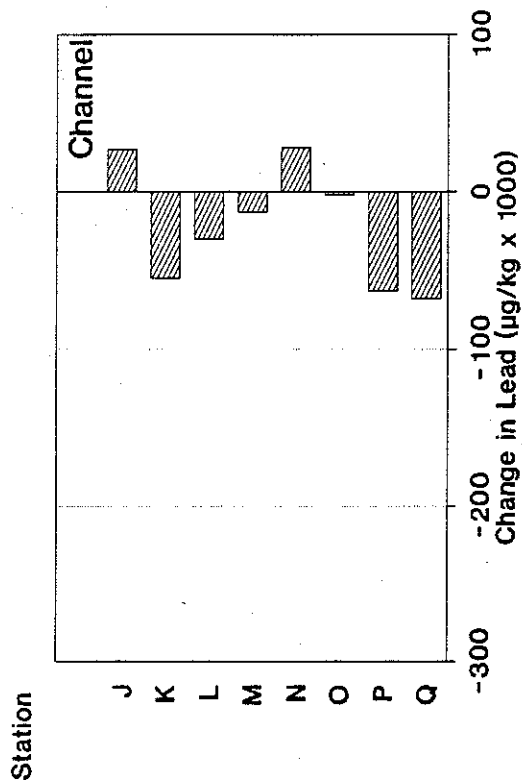
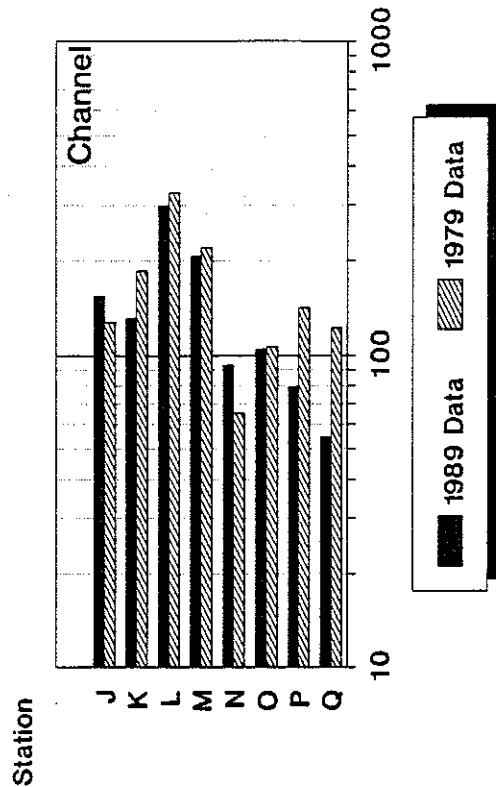
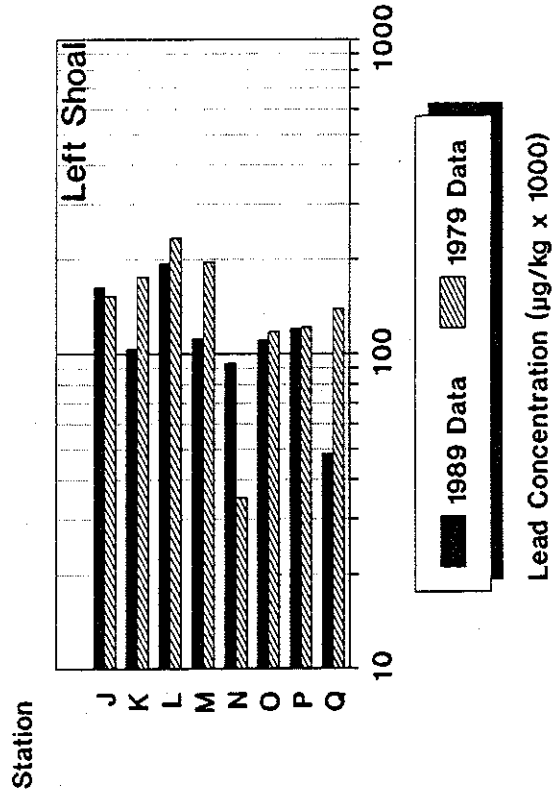


Figure 39. Comparison of lead concentrations in Elizabeth River sediments between 1979 and 1989.

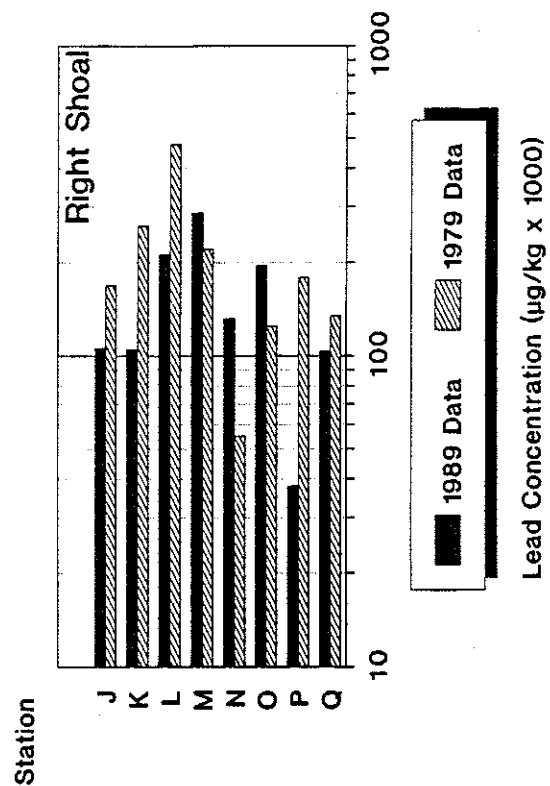
LEAD IN ELIZABETH RIVER SEDIMENTS



LEAD IN ELIZABETH RIVER SEDIMENTS



LEAD IN ELIZABETH RIVER SEDIMENTS



recent sediments are generally less contaminated than deeper sediments.

Mercury

The mean concentration of mercury in Elizabeth River sediments was approximately three times higher in 1989 than in 1974 (Table 8). Unfortunately, this metal was not analyzed in sediment samples collected in the 1979 study, thus statistical comparisons to 1989 data were not possible.

Nickel

Nickel was not analyzed in the Johnson and Villa (1976) study of metals in sediments of the Elizabeth River. On the whole, the nickel concentrations in sediment changed only marginally ($p=0.06$), from a grand mean of 34.7 mg/kg in 1979 to 25.1 mg/kg in 1989 (Figs. 40, 41). Consistent decreases were observed at Sites K, L, P, and Q. However, it should be noted that the latter two sites were dredged shortly before the samples for the 1989 study could be taken, so this pattern should be interpreted accordingly. The Site M right shoal sample displayed an elevated level of nickel, possibly associated with shipyard activities. The distribution of nickel with depth (Fig. 18) tends to substantiate all of these temporal patterns.

Zinc

The mean concentration of zinc in Elizabeth River sediments was 379 mg/kg in 1974 (Johnson and Villa, 1976) (Table 8). Zinc in surface sediments showed no overall statistically significant

changes ($p=0.27$) between 1979 (379 mg/kg) and 1989 (387 mg/kg) (Figs. 42, 43). Consistent decreases were observed for Sites J and K, while the transects for Sites L, M, and P produced mixed results. These temporal patterns are confirmed by the depth distribution of zinc for these regions (Fig. 21). Site N samples were consistently higher in zinc concentrations in the 1989 study, while Site Q samples were lower, as may be expected due to the recent dredging activities.

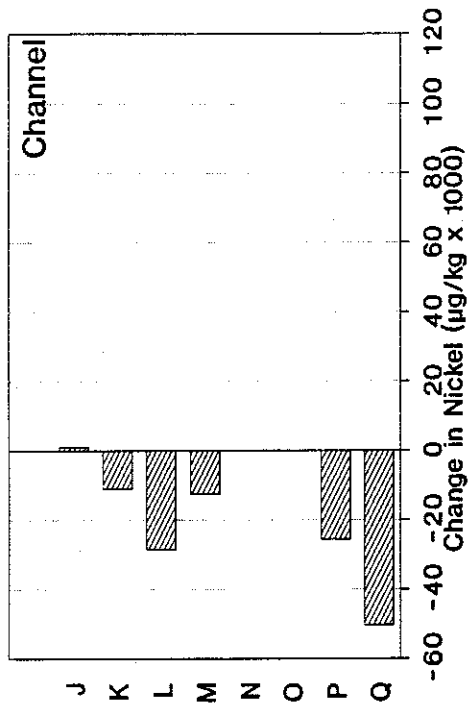
In summary, five of the metals (Cd, Cr, Fe, Ni, and Pb) appeared to decrease in the sediments of the study area. The other two metals (Cu, Zn) displayed no significant overall changes. Although the sediments of certain regions of the Elizabeth River remain highly contaminated with metals, the apparent decrease in many of the metals may be associated with pollution control actions.

Two regions appeared to display increases in a number of the metals in surface sediments: Site M, right shoal in the vicinity of a major shipyard; and Site N near the mouth of Paradise Creek.

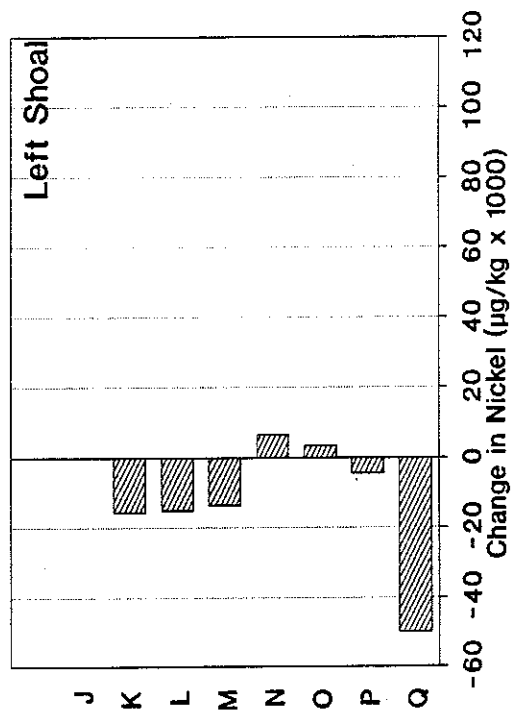
Figure 40. Change in nickel concentrations in Elizabeth River sediments from 1979 to 1989.

CHANGE IN NICKEL CONCENTRATIONS IN SEDIMENTS FROM 1979 TO 1989

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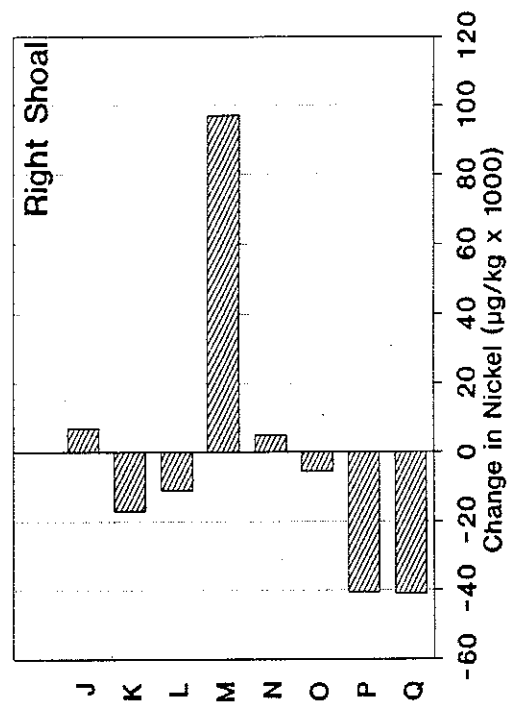
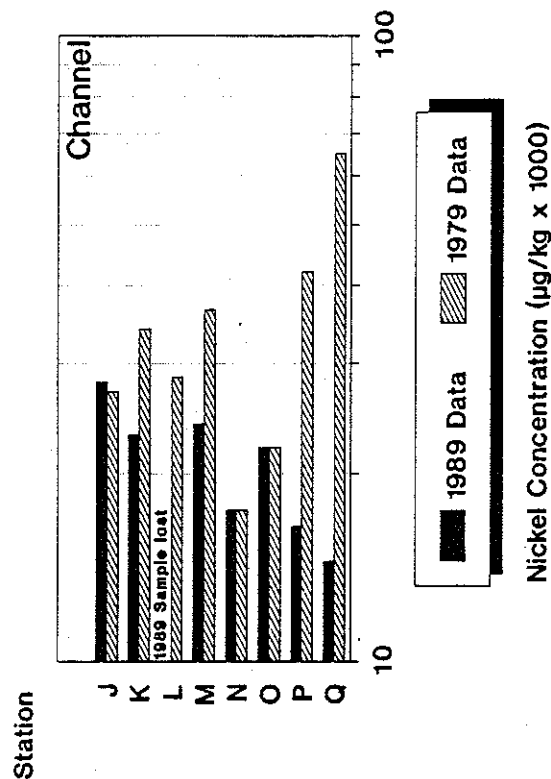
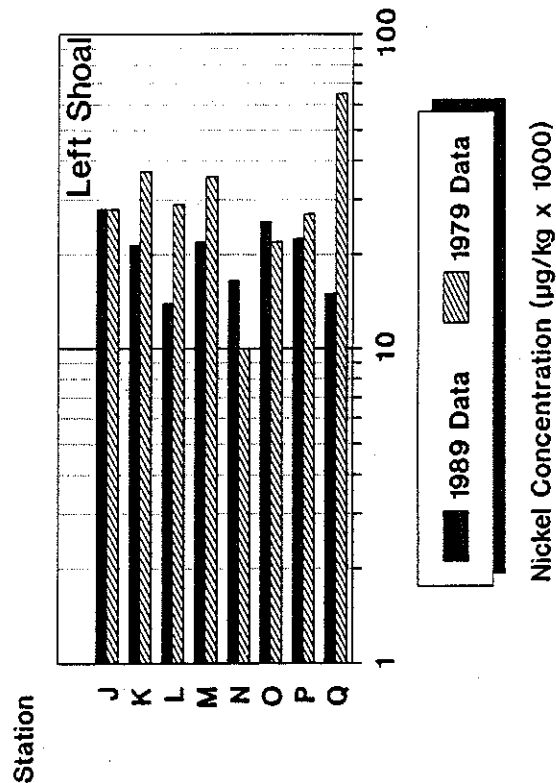


Figure 41. Comparison of nickel concentrations in Elizabeth River sediments between 1979 and 1989.

NICKEL IN ELIZABETH RIVER SEDIMENTS



NICKEL IN ELIZABETH RIVER SEDIMENTS



NICKEL IN ELIZABETH RIVER SEDIMENTS

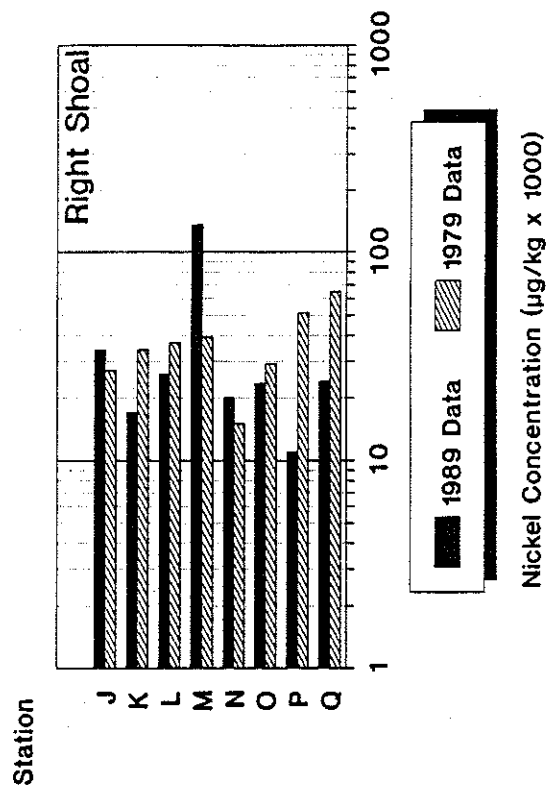
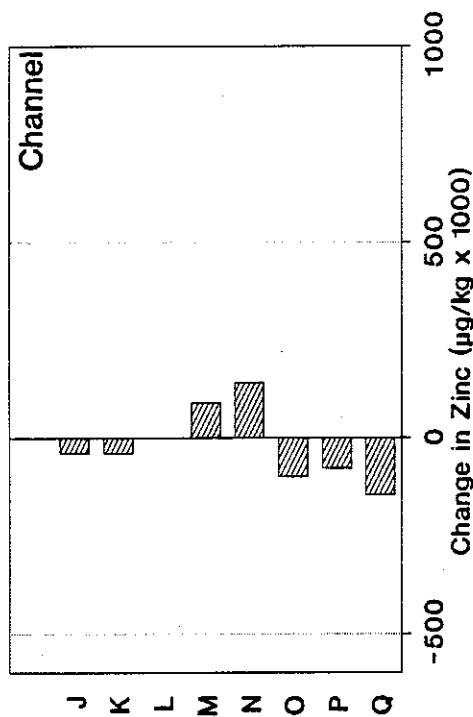


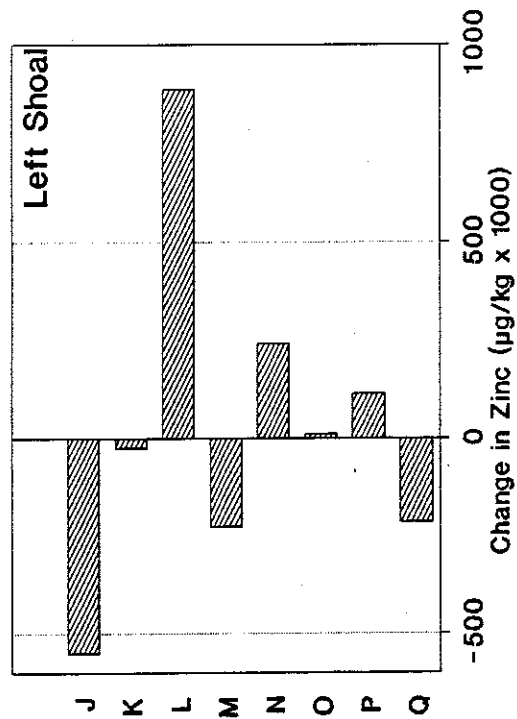
Figure 42. Change in zinc concentrations in Elizabeth River sediments from 1979 to 1989.

CHANGE IN ZINC CONCENTRATIONS IN SEDIMENTS FROM 1979 TO 1989

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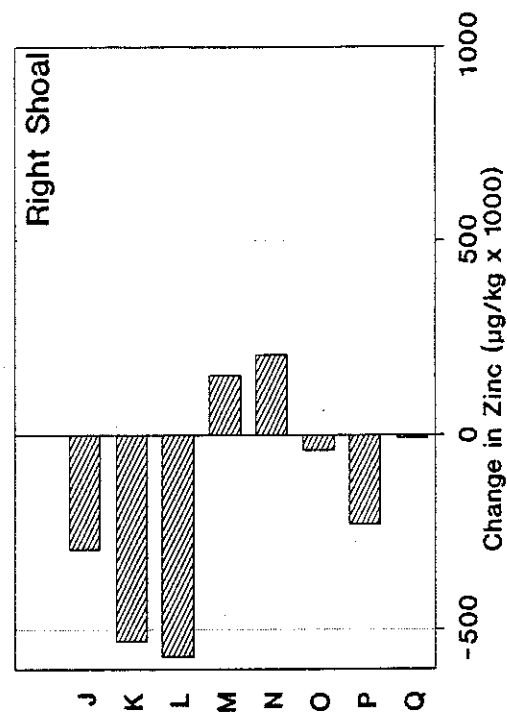
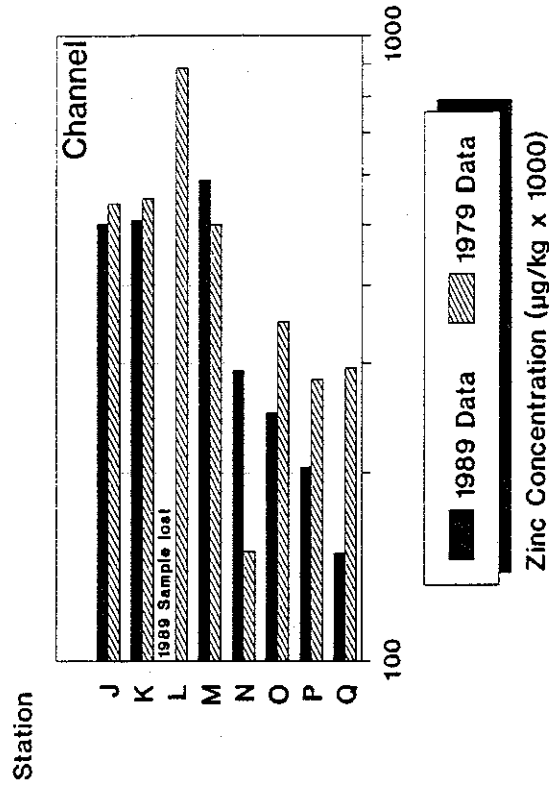
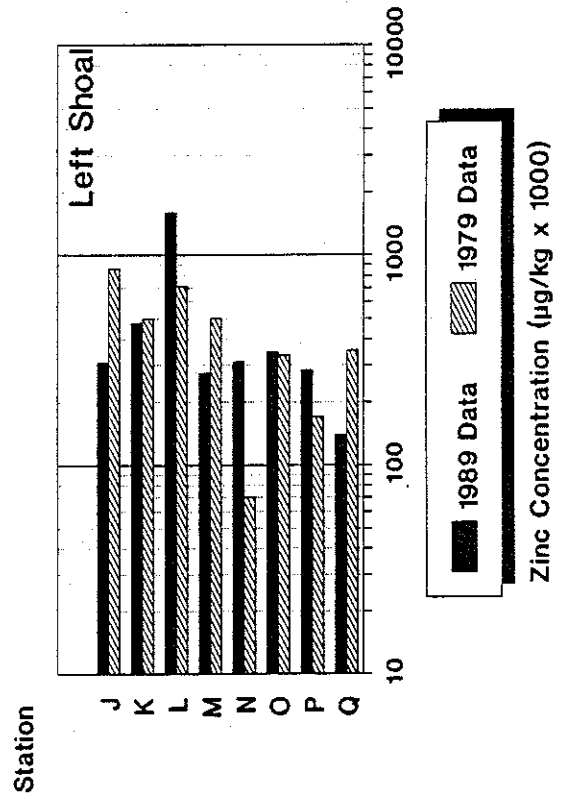


Figure 43. Comparison of zinc concentrations in Elizabeth River sediments between 1979 and 1989.

ZINC IN ELIZABETH RIVER SEDIMENTS



ZINC IN ELIZABETH RIVER SEDIMENTS



ZINC IN ELIZABETH RIVER SEDIMENTS

